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WATER-POLLUTION CONTROL IN THE PRIMARY NONFERROUS-METALS INDUSTRY. VOLUME II. ALUMINUM, MERCURY, GOLD, SILVER, MOLYBDENUM, TUNGSTEN

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WATER-POLLUTION CONTROL IN THE PRIMARY NONFERROUS-METALS INDUSTRY -- VOLUME II. ALUMINUM, MERCURY, GOLD, SILVER, MOLYBDENUM, AND TUNGSTEN,

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The trend in the primary aluminum industry is toward reduced or zero discharge of waste water from both alumina refineries and aluminum smelters. The principal treatment needs of the aluminum industry relate to common types of industrial waste water such as cooling tower blow-down and neutralization products, and the specialized need to remove or recover fluoride ion components from fume scrubbers at smelters. The primary mercury industry, by virtue of a current air pollution control problem, may require increased measures of water pollution control associated with air emission control equipment or new processing methods. The primary molybdenum industry, consisting of a small number of operations other than those associated with the copper industry, has taken or is designing effective methods of water pollution control ranging from isolated water systems to changes in flotation reagent concentrations. Plants processing refractory metal concentrates to end products generally are associated with municipal water systems and show high materials recoveries with concurrent close control and careful segregation of waste water streams. Neutralization with filtration of acid wastes is a common practice of the plants surveyed. The small amount of information available for the primary gold and silver industries shows greatly differing practices, ranging from zero discharge in arid climates to problems with mercury and cyanide contents in waste waters. (See also W74-05116)((EPA)

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September 1973

WATER-POLLUTION CONTROL IN THE PRIMARY NONFERROUS-METALS INDUSTRY

VOLUME II. ALUMINUM, MERCURY, GOLD, SILVER, MOLYBDENUM, AND TUNGSTEN

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ABSTRACT

Volume II of this study deals with the processes and water practices in the aluminum, mercury, gold, silver, molybdenum, and tungsten industries. Data obtained from the producers of these metals showed the patterns and amounts of water usage for different purposes within these types of plants and the degrees and types of waste water either controlled, treated, or discharged to various receiving waters. Water usage and recirculation were found to be highly variable among the individual plants, with some practices being associated with climate and water costs.

The trends in waste-water control varied with the individual industries. Alumina refineries and aluminum smelters apparently are moving toward zero or decreased discharge despite installation of increased production capacity. Water practices in the primary mercury industry reflected the remote location and arid climates associated with these operations. The need for air-pollution control in the mercury industry possibly may require new equipment or processes, with associated needs for water-pollution-control measures. The balance of the operations studied showed individual characteristics varying as much as their locations, which ranged from remote desert to municipal locations.

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SECTION I

CONCLUSIONS

1. The trend in the primary aluminum industry is toward reduced or zero discharge of waste water from both alumina refineries and aluminum smelters.

2. The principal treatment needs of the aluminum industry relate to common types of industrial waste water such as cooling tower blow-down and neutralization products, and the specialized need to remove or recover fluoride ion components from fume scrubbers at smelters.

3. The primary mercury industry, by virtue of a current air pollution control problem, may require increased measures of water pollution control associated with air emission control equipment or new processing methods.

4. The primary molybdenum industry, consisting of a small number of operations other than those associated with the copper industry, has taken or is designing effective methods of water pollution control ranging from isolated water systems to changes in flotation reagent concentrations.

5. Plants processing refractory metal concentrates to end products generally are associated with municipal water systems and show high materials recoveries with concurrent close control and careful segregation of waste water streams. Neutralization with filtration of acid wastes is a common practice of the plants surveyed.

6. The small amount of information available for the primary gold and silver industries shows greatly differing practices, ranging from zero discharge in arid climates to problems with mercury and cyanide contents in waste waters.

SECTION II

RECOMMENDATIONS

Based on the findings of this study, it is recommended that:

1. Studies be carried out on the removal and reclamation of fluoride components from the wet-gas-scrubber liquors used in aluminum smelters.

2. Current and future developments in the primary mercury industry be monitored and evaluated to allow timely development of water pollution control practices applicable either to wet methods of air emissions control, or to waste waters generated by new hydrometallurgical processes.

3. Further insight be obtained into tungsten ore concentrating operations to identify specific needs in terms of geographical location, intermittent operation, and the disposal or treatment of waste leaching liquors.

4. A more intensive study be conducted directed at obtaining data on individual unit process waste sources, and that such a study include some provision for sampling and analysis. This work should be aimed at defining point sources, characteristics, volumes, unit waste loads and the effectiveness of treatment practice in more detail than this study has shown to be presently available.

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SECTION III

INTRODUCTION

The purposes of this study are to assess current water-pollution-control practices and problems and to provide a basis for recommending specific directions to develop water-pollution-control methods in the nonferrous-metals industry. The approach used in this study has been to deal with specific practices and problems rather than with generalities or overall considerations. This study, in attempting to be specific, thus has dealt with the variegated and individualistic nature of the metal-producing operations which constitute the total industry.

This report is organized to present the data obtained in groupings which are determined by the relationships between production operations. Thus, Volume I dealt with the production processes and water-use practices of the copper, lead, and zinc industries. These major metal-plant operations include the manufacture of the following by-products: cadmium, "by-product" gold, silver, platinum, palladium, and rhodium; arsenic, bismuth, thallium, indium, selenium, tellurium, and molybdenum concentrates or oxides; antimony; and the metal compounds arsenic trioxide, copper sulfate, nickel sulfate, zinc oxide, zinc sulfate, and sulfuric acid. This volume (Volume II) deals with operations producing alumina and aluminum, mercury, primary gold and silver, and molybdenum and tungsten.

In preparing this report, it was found necessary to deal with manufacturing processes in a somewhat intensive manner in order to identify the process steps which produce characteristic components of waste water; i.e., in some cases the primary metal product is so efficiently extracted that little waste is generated, whereas marginal discharges of by-product operations or nominally minor components of raw materials appear in waste streams.

The method used in the study was to assemble the often fragmentary information available in the literature and, more importantly, to obtain information directly from the industry. The letters of inquiry sent to selected companies requested information on current practices of water usage, and the sources, characteristics, and amounts of waste water, and the industry's own statements of problem areas and treatment needs. Two constraints were applied to the data supplied by industry: that such information be supplied voluntarily and at the expense of industry, and that the specific sources of each lot of information remain anonymous.

In reporting the results of this study, separate sections have been devoted to each metal or metal grouping. The size and distribution of the particular industry, its economic characteristics, the technology employed, its water-usage characteristics, its waste-collection, treatment,

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and disposal practices, and anticipated future treatment requirements are discussed in each section.

SECTION IV

PROCEDURES

The sequence of tasks in this program consisted of:

1. Compilation of a list of the companies and plant facilities in the United States which produce nonferrous metals

2. Contacting the identified companies by telephone, letter, or personal visits to obtain the desired information

3. Compilation and analysis of the data obtained to prepare this report

4. Use of documentary sources wherever available to obtain required associated information such as industry structure, overall economic aspects, process technology, prior studies on water usage, and other supplementary information.

The open literature was found to contain little specific information on water problems or treatment in the nonferrous industry. This study, therefore, placed its main reliance for specific details on the voluntary contributions of unpublished data from industry. Further, it was found that the degree of precise knowledge of plant water usage is still highly variable from plant to plant.

Out of 56 companies approached, about 50 percent responded by submitting data in varying degrees of detail. Their replies covered 78 facilities ranging from single mine operations to complexes of mines, mills, smelters, refineries, etc. The responses received provided information on 35 mines, 33 concentrators, 8 copper leach-precipitation operations, 27 copper, lead, and zinc smelters, 20 refineries, 8 sulfuric acid plants, and 8 power plants. This group of operations is reported on in Volume I.

Also, responses were obtained on 3 alumina refineries, 11 aluminum smelters, 3 primary mercury mining and furnace operations, 2 mines producing gold and/or silver, and 4 refractory-metal processing plants. These processes and associated water use and treatment practices are discussed in Volume II.

In view of the extreme complexity of the nonferrous-metals industry and recognizing that many who use this report may be unfamiliar with the industry, it was decided that each section should include a more or less detailed description of the industrial segment, its structure, and technology, as an aid to understanding and interpreting its water and waste-treatment problems and practices.

SECTION V

THE PRIMARY ALUMINUM INDUSTRY

Characteristics and Geographical Distribution

The major characteristics of the primary aluminum industry of the United States and its processing operations may be briefly indicated as:

1. The importation of most of its principal raw material, bauxite ore, from overseas sources

2. The refining of bauxite ore to an intermediate product, anhydrous alumina, at the points of entry on the coastline

3. The location of metal-reduction plants near sources of low-priced electrical power.

The primary aluminum industry in the United States may be considered to consist of two segments, the alumina-refining plants and the aluminum-reduction works.

The alumina-refining plants operated by the various United States aluminum producers, their capacities, and their locations are indicated in Table 1 and Figure 1. These plants process raw bauxite ore to the

TABLE 1. OPERATING COMPANIES, LOCATIONS, AND CAPACITIES OF U.S. ALUMINA REFINING PLANTS (1)

Company	Plant Location	Capacity, thousands short tons/year
Aluminum Company of America	Mobile, Alabama	950
	Bauxite, Arkansas	400
	Point Comfort, Texas	900
Kaiser Aluminum & Chemical Corp.	Baton Rouge, Louisiana	985
	Gramercy, Louisiana	620
Reynolds Metals Company	Hurricane Creek, Arkansas	840
	La Quinta, Texas	1,185
Ormet Corporation	Burnside, Louisiana	550

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FIGURE 1. LOCATION OF ALUMINA REFINING PLANTS IN THE U.S.

intermediate product form of refined alumina. In 1966, these plants accounted for the refining of 2,000,000 short tons of domestic bauxite and 12,700,000 short tons of imported bauxite. The dollar value of these ores is difficult to express because in many cases the bauxite mine, shipping means, and alumina refinery are related either by common ownership or trading arrangements between operations. By 1968, these plants were refining about the same amount of domestic ores and approximately 12,000,000 short tons of imported bauxite, and, in addition, 1.8 million tons of alumina were imported. The recent trend has been to reduce the volume of material shipped by refining the bauxite ore to alumina overseas (a 2 to 1 reduction in shipping weight), at, for example, the Harvey Aluminum Company's refinery in the Virgin Islands (350,000 tons per year) or the refinery at Queensland, Australia.

The ownership, location, and size of current and future aluminum-reduction plants are shown in Table 2.[2,3] The locations of these plants are indicated on the map in Figure 2.

The reasons for the geographical distribution of the aluminum reduction plants may be illustrated by the following values of delivered cost of alumina and electrical power[4]:

Geographical Area	Shipping Cost per Ton of Alumina, $	Power Cost, mils/kwhr
Pacific Northwest		
By ocean	5.00	2.1
By rail	12.26	2.1
Ohio Valley	8.95	3.5
Tennessee Valley	5.35	4.2

These figures serve to explain the trend toward the opening of new plants in the Tennessee Valley and Pacific Northwest areas. The increasing rate of expansion of the Australian ore reserves and alumina refineries, which would supply the Northwest area, is another factor to be considered in future trends in aluminum-plant location.

That is, the availability of cheap electrical power, usually from hydroelectric generators, or, alternatively, from natural-gas-fueled generators as in the Gulf Coast area, must be balanced against the shipping cost of the refined alumina and other raw materials to the smelter, and the shipping cost of the aluminum ingots to markets.

Contribution to United States Economy

The contribution of the primary aluminum industry to the economy may be expressed in two ways: dollar values and product usefulness. According to statistics for 1967, the primary aluminum industry was described in the following economic terms.[5]

TABLE 2. OWNERSHIP, LOCATION, AND PRODUCTION CAPACITY OF U.S. PRIMARY ALUMINUM PLANTS [2,3]

	Capacity, short tons/yr	
	Installed, 1969	Planned, 1973
Aluminum Company of America		
Alcoa, Tennessee	200,000	275,000
Badin, North Carolina	100,000	100,000
Massena, New York	125,000	125,000
Point Comfort, Texas	175,000	175,000
Rockdale, Texas	225,000	275,000
Vancouver, Washington	100,000	100,000
Warrick, Indiana	175,000	275,000
Wenatchee, Washington	175,000	175,000
Totals	1,275,000	1,500,000
American Metals Climax		
Warrenton, Oregon		150,000
Anaconda Aluminum Company		
Columbia Falls, Montana	175,000	175,000
Sebree, Kentucky	--	295,000
Consolidated Aluminum Corporation		
New Johnsonville, Tennessee	140,000	140,000
Eastalco Aluminum Company		
Frederick, Maryland	--	255,000
Gulf Coast Aluminum Company		
Lake Charles, Louisiana	--	35,000
Harvey Aluminun (Inc.)		
The Dalles, Oregon	87,000	87,000
Cliffs, Washington	--	191,000
Intalco Aluminum Corporation		
Bellingham, Washington	265,000	265,000
Kaiser Aluminum & Chemical Corporation		
Chalmette, Louisiana	260,000	260,000
Mead, Washington	206,000	206,000
Ravenswood, West Virginia	163,000	163,000
Tacoma, Washington	81,000	81,000
Totals	710,000	710,000
National-Southwire Aluminum Company		
Hawesville, Kentucky	--	180,000

Continued on following page.

TABLE 2. (continued)

	Capacity, short tons/yr	
	Installed, 1969	Planned, 1973
Noranda		
New Madrid, Missouri	--	75,000
Northwestern Aluminum Company		
Warrenton, Oregon	--	135,000
Ormet Corporation		
Hannibal, Ohio	240,000	240,000
Revere		
Scottsboro, Alabama	--	112,000
Reynolds		
Arkadelphia, Arkansas	63,000	63,000
Jones Mills, Arkansas	122,000	122,000
Listerhill, Alabama	221,000	221,000
Longview, Washington	190,000	190,000
Massena, New York	128,000	128,000
San Patricio, Texas	111,000	111,000
Troutdale, Oregon	100,000	100,000
Unidentified by Plant	--	40,000
Totals	935,000	975,000
U.S. Totals	3,827,000	5,520,000

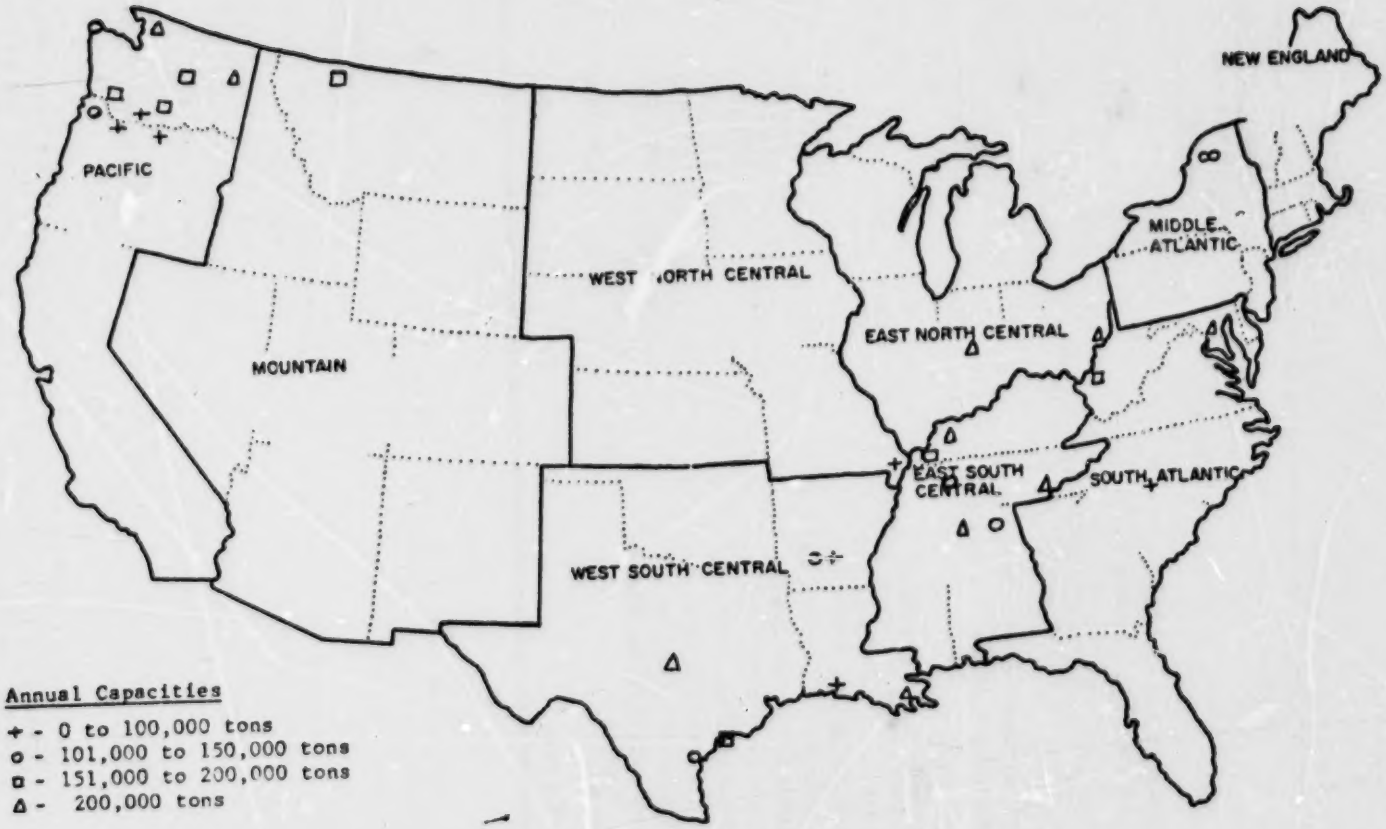

FIGURE 2. LOCATIONS OF ALUMINUM REDUCTION PLANTS

Number of Establishments	25
Number of Employees	23,800
Payroll	$190,900,000
Value of Shipments	$1,608,700,000
Materials Consumed	
Alumina	5,692,500 short tons
Alumina	$365,600,000
Other	$271,800,000
Purchased Electrical Energy	
Million kwhr	41,956.0
Million dollars	143.6
Primary Aluminum Produced	6.54 billion pounds
Total Consumption	8.3 billion pounds
Per-Capita Consumption	42 pounds

In this listing the difference between primary production and total consumption is due to secondary metal recovery and imports.

The primary aluminum industry produces only a raw material for other manufacturers. The distribution of aluminum in its final product forms may be indicated as follows:(6)

Major Market Area	Shipments, millions of pounds	Share of Market
Transportation	1,915	21.4
Building and Construction	1,866	20.8
Electrical	1,249	13.9
Containers and Packaging	866	9.7
Consumer Durables	844	9.4
Machinery and Equipment	625	7.0
Exports	657	7.3
Others	940	10.5
	8,962	

It is estimated that there are about 4000 end-use forms for aluminum. Only an indication can be given of these final uses in this report. The commercial forms of aluminum and aluminum alloys include

Castings	Structural shapes
Sheet and plate	Tube and pipe
Foil	Forgings
Wire, rod, and bar	Impact extrusions
Extrusions	Particles, powder, and paste

The final applications of aluminum include and far exceed those indicated in the following listing(6):

> Building Construction -- siding, gutters and downspouts, awnings, doors, windows, insulation, curtain walls, ornamental metalwork, railings, roofing

High Products -- bridges and railings, guard rails, signs, light standards, fencing, culvert

Electrical Structures -- towers, crossarms, switchyard support and sheltering structures

Petroleum Industry -- drill rigs, offshore structures, drill pipe, storage tanks, pipelines

Chemical, Food, Drug, and Beverage Industry -- corrosion-resistant tanks, bins, pipe, stills, condensers, trays, heat exchangers, tank cars, valves, fittings, rolls, buckets, spools

Structures and Equipment for Refrigeration and Cryogenic Applications

Automotive and Engine Applications -- cylinder blocks, heads, bearings, engine covers, connecting rods, pistons, superchargers, transmission cases, wheels, housings, trim, hardware, fuel tanks, truck chasis, frames, and bodies, panels, tank trucks

Railroad Equipment -- tank cars, hopper cars, buildings, car panels, signs, signals

Marine Applications -- protective anodes, buoys, hydrofoils, small craft, gun boars, canoes, barges, engine blocks

Aircraft and Aerospace Applications -- aircraft, airframes, skins, panels, forgings, engine components, honeycomb panels, castings, helicopter rotor blades, propellers, missile skins, frames, and fuel tanks, space vehicles, ground support and test equipment

Military Vehicles and Equipment -- armor plate, wheeled vehicles, mobile equipment, wheels, amphibious vehicles, portable bridges, rocket and grenade launcher tubes

Machinery, Tooling and Instrument Applications -- bearing alloys, pumps, tire molds, patterns, tooling plate, assembly jigs, irrigation pipe, business-machine covers, nonmagnetic instrument cases and components, materials-handling equipment, mining equipment, textile machinery, printing machinery

Electrical and Electronic Equipment -- wire, cable, bus bar, power transmission and distribution equipment, towers, capacitors, conduit, antenna, lighting reflectors

Household Goods -- appliances, furniture, etc.

Packaging Applications -- cans, foil packages, collapsible tubes, bottle caps

Pigment and Paint Applications.

Projected Growth of the Industry

The history of the output of the primary aluminum industry is indicated in Figure 3.[6,7] Shown for comparison are the data for mill-product shipments for the years 1960 to 1970. Various analyses have found growth rates for the aluminum industry to be a compounded annual growth rate of 5.8 percent over the last 20 years for primary production and a 10 percent annual growth rate for the total consumption of aluminum mill products and other forms. At the end of 1969, one projected growth rate was estimated at 7 percent a year, or nearly 16 billion pounds of mill products by 1975.[7] Unless patterns change, this would call for 9.9 billion pounds of primary production in 1973, and 12 billion pounds in 1975. Currently planned expansions in primary production (Table 2) also agree with the forecasts of 7 to 10 percent annual expansion rate. It appears that estimates of future growth fall within the range of 5.8 percent (based on the past 20 years) to 10 percent (based on the past 10 years).[7,8]

Raw Materials and Process[9-11]

The raw materials used in the production of 1 pound of aluminum metal are:

Input to Alumina Plant
- 4 pounds bauxite ore
- 0.2 pound soda
- 0.2 pound limestone
- 0.5 pound coal
- 0.25 pound fuel oil

Input to Aluminum Plant
- 2 pounds alumina
- 0.25 pound pitch
- 0.5 pound petroleum coke
- 0.1 pound cryolite
- 0.04 pound aluminum fluoride
- 0.6 pound baked carbon
- 10 kilowatt hours of electrical energy.

The following discussion deals briefly with the most important of these raw materials and where they are used in the production processes.

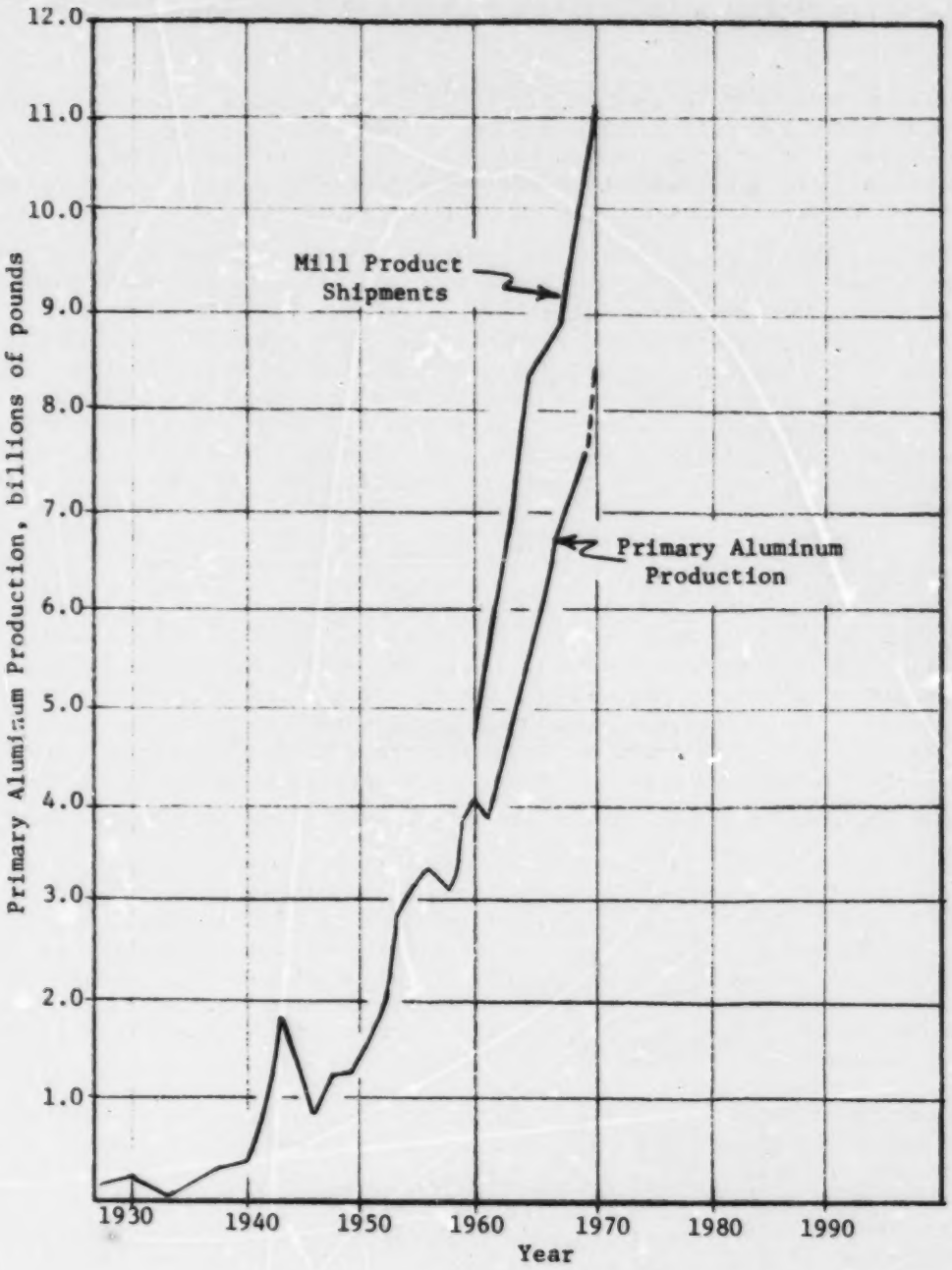

FIGURE 3. PRIMARY ALUMINUM PRODUCTION AND MILL PRODUCT SHIPMENTS FOR SELECTED SPANS OF YEARS (6)(7)

Types and Sources of Bauxite Ores

Bauxite ores vary in characteristics from stony materials to soft clays. In general, the term bauxite applies to weathered deposits from which substances other than alumina have been leached to leave a high enough alumina content to make the deposit profitably workable. The compositions of bauxite ores usually fall within the following ranges:

Material	Content, weight percent
Al_2O_3	40 to 60
SiO_2 free and combined	1 to 5
H_2O combined	12 to 30
Fe_2O_3	7 to 30
TiO_2	3 to 4
F, P_2O_5, V_2O_5, other	0.05 to 0.20

The principal determinants characterizing a bauxite ore are the form of hydrate in which the alumina occurs and the form in which the silica occurs. The alumina may be present as a monohydrate, indicated by the formula $Al_2O_3 \cdot H_2O$, and, as such, may take either of two mineralogical forms, identified as boehmite or diaspore, or may be present as the trihydrate indicated by $Al_2O_3 \cdot 3H_2O$, taking forms known as gibbsite or hydragillite. The principal distinction between the two hydrated forms is that the trihydrate forms are more soluble than the monohydrate in the solvent (sodium hydroxide or sodium carbonate solution) used in the refining process.

The silica content and the form in which it is present are important factors in the yield of a bauxite ore. On a weight basis, one part of silica ties up one part of alumina in the form of the mineral kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, and, additionally, results in the consumption of one part of the caustic solution in the formation of insoluble sodium aluminum silicate. The use of high-silica bauxites involves either the above losses or the use of a two-step, "combination" process to recover the losses in the initial processing.

Deposits of bauxite ores are found worldwide, as shown by the listing of estimated ore reserves in Table 3. Of more specific interest is the listing of Table 4 which shows the sources of ore used by the United States aluminum industry and the specific alumina-refining plants processing the ores. The geographical locations of the alumina refineries were shown in Figure 1. It should be noted that the United States aluminum industry obtains two types of raw materials from overseas: bauxite ore and refined alumina. Some comparative figures showing the domestic production of bauxite and imports of bauxite and alumina for related years are given in Table 5.

Thus, in brief, the sources of bauxite ores are overseas except for a

TABLE 3. ESTIMATED WORLD ORE RESERVES OF BAUXITE[4]

Region	Country	Estimated Ore Reserves, millions of tons	Present Status of Utilization
Europe	France	100	Used in France
	Spain	Some	Unexploited
	Italy	Some	Used in Italy (with imports)
	Yugoslavia	100	Exported to Germany and Italy
	Austria	Some	
	Hungary	~100	Exported to U.S.S.R.
	Rumania	10-20	Unexploited
	Greece	50-100	Exported to Western Germany and U.S.S.R.
	Turkey	~10-50	Unexploited
Americas	United States	~50	Supplies 20% of U.S. consumption
	British Guiana	Several hundred	Exported to U.S.
	Dutch Guiana Surinam	Several hundred	Exported to U.S.
	French Guiana	40	Unexploited
	Caribbean Islands	300	Exported to U.S. and Canada
	Haiti and Dominican Republic	5-10	Exported to U.S. and Canada
	Jamaica	200-300	Exported to U.S. and Canada
	Brazil	~100-150	Little information available
U.S.S.R.	U.S.S.R.	4-5	Lacks bauxite; uses nepheline
Africa	Guinea	200-100	Current production exported to U.S. and Europe
	Mali		Large deposits found
	Ghana	200	Exported to Britain and Germany
	Cameroons	500-1000	--
	Congo Republic	10-50	Unexploited
Asia	India	100-200	--
	Malaysia and Indonesia	10-50	Exported to Japan
	Tonkin	Small	
	China	Information uncertain	
	Australia	1000	Exported worldwide

TABLE 4. SOURCES OF BAUXITE AND LOCATIONS OF ALUMINA PLANTS SUPPLYING THE U.S. ALUMINUM INDUSTRY

Source of Bauxite	Locations of Alumina Refining Plants
Arkansas	Bauxite, Arkansas Hurricane Creek, Arkansas
Australia	Queensland, Australia
Dominican Republic	Point Comfort, Texas
Guinea	St. Croix, Virgin Islands
Haiti	Corpus Christi, Texas
Jamaica	Point Comfort, Texas Baton Rouge, Louisiana Gramercy, Louisiana Corpus Christi, Texas
Surinam	Mobile, Alabama Point Comfort, Texas Burnside, Louisiana

TABLE 5. COMPARATIVE FIGURES SHOWING IMPORTS AND DOMESTIC PRODUCTION OF BAUXITE AND ALUMINA FOR THE U.S. ALUMINUM INDUSTRY

Year	Source	Bauxite, millions of short tons		Alumina, millions of short tons
1960	U.S.	2.24		--
	Imports	9.75		0.089
1968	U.S.	1.86		--
	Imports	12.32		1.345
1969	U.S.	2.20		--
	Imports	13.45		1.8
	Jamaica	∿8.06	Australia	∿1.2
	Surinam	∿2.69	Surinam	∿0.45
	Dominican Republic Haiti Guyana	balance	Other sources	balance

single deposit within the United States, in Arkansas, which is mined at a rate of about 2 million short tons per year. The balance of the bauxite requirements are supplied from overseas. A recent trend in this pattern is the establishment of alumina-refining plants at overseas sites (Jamaica and Queensland) and the importation of the refined alumina. The relatively recent development and exploitation of bauxite reserves in Australia and the construction of refining plants there will continue to have an increased effect on the import pattern in the near future.

The sources of bauxite and alumina have been discussed above. Of the other required raw materials, most are obtained from conventional commercial sources. Two of the materials--cryolite and aluminum fluoride--are especially noteworthy because removal of their fluoride contents accounts for the major use of water in gas scrubbers in aluminum-reduction plants. Cryolite and aluminum fluoride are the major materials used to form a fused-salt electrolyte in which alumina is dissolved and electrolyzed to produce aluminum metal.

Cryolite is a white crystalline material with the chemical formula $AlF_3 \cdot 3NaF$. Natural cryolite has been found in only one location, Greenland, and exhibits major constituents as follows:

Fluorine, F	51 weight percent
Sodium, Na	30 weight percent
Alumina, Al_2O_3	12.5 weight percent.

The output of natural cryolite is limited and it is used only during the starting period in the operation of the electrolytic cell because it is apparently more stable than the synthetic form. Synthetic cryolite is used during the operating period of the cell and is produced by chemical processes having as the principal reaction:

$$Al_2O_3 \cdot 3H_2O + 12HF + 6NaOH \rightleftarrows Na_3AlF_6 + 12H_2O.$$

Aluminum Trifluoride, AlF_3, also is a product of chemical processing and is used in great quantities by the aluminum industry.

Major Processes in the Production of Aluminum[9,10,11]

The major processing operations discussed in the following sections are shown on the flowsheet in Figure 4.

The refining of alumina from bauxite is accomplished by either of two processes: one called the Bayer process, the other the combination process.

In the Bayer process, the bauxite ore is dried and ground prior to chemical treatment. The hydrated alumina in the bauxite is converted

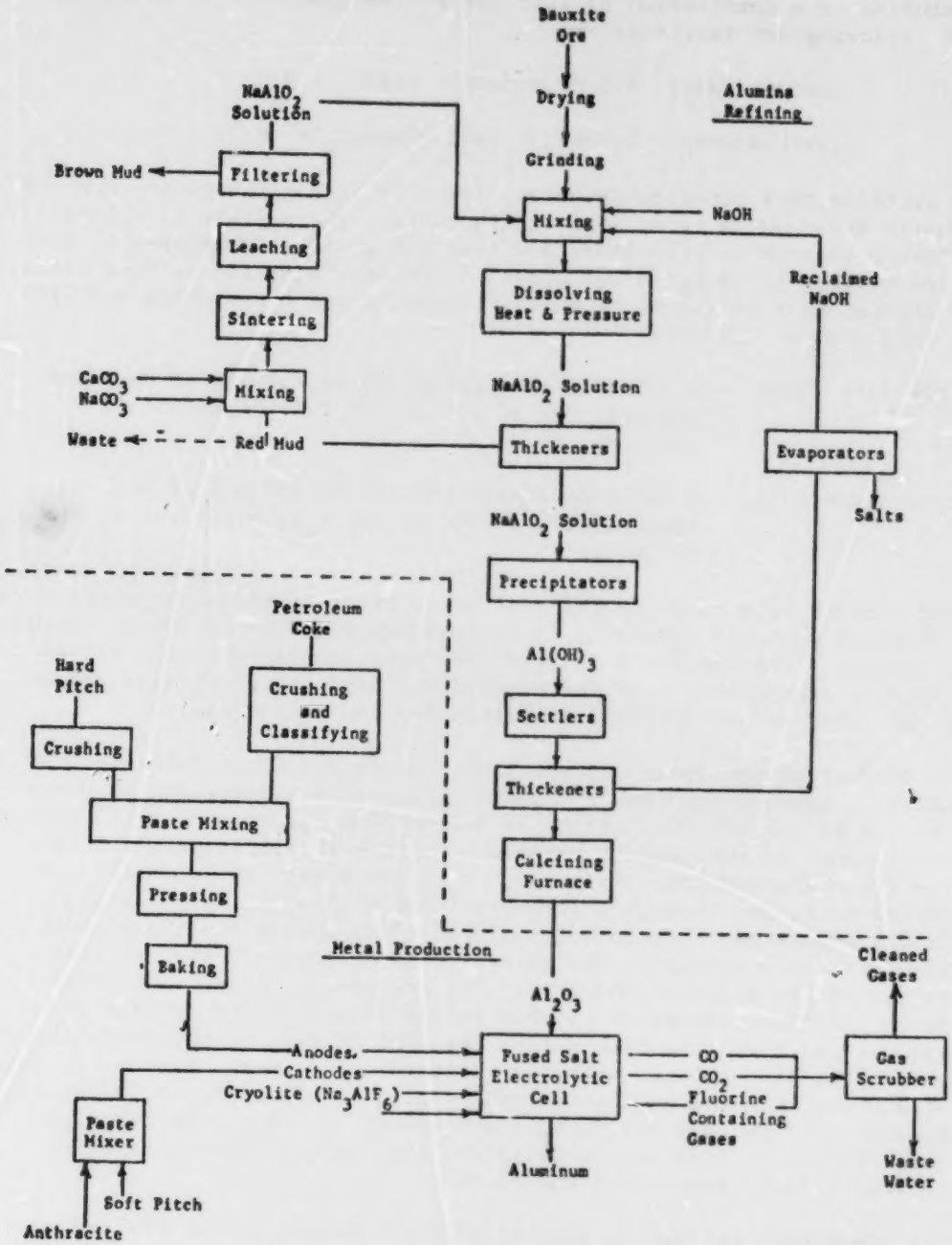

FIGURE 4. FLOWSHEET OF MAJOR PROCESSES IN ALUMINUM PRODUCTION

to a soluble salt, sodium aluminate, by reaction with either sodium hydroxide or a combination of lime and sodium carbonate to accomplish the following net reaction:

(monohydrate) $AlO\text{-}OH + NaOH \rightarrow NaAlO_2 + H_2O$

(trihydrate) $Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$.

In practice this reaction is accomplished by mixing the ground ore with caustic solution in large iron mixing tanks. The mixture is fed into pressure vessels or autoclaves and heat and pressure developed by either steam heating of jacketed autoclaves or direct injection of live steam. Conditions must be varied to suit the bauxite ore composition but may be indicated as follows:

Trihydrate forms - a solution containing 100 to 150 g/l of Na_2O and temperatures of 120 to 170 C at 50 to 70 psi pressure

Monohydrate forms - a solution containing 200 to 300 g/l of Na_2O and temperatures of 200 to 250 C at pressures as high as 500 psi.

Most bauxite ores contain different proportions of the monohydrate and trihydrate ores and operating conditions are adjusted to obtain optimum processing. The greater portion of bauxites processed in the United States is predominantly of the monohydrate form, which permits the use of the lower concentrations, temperatures, and pressures.

The product of the above digestion process is a slurry containing $NaAlO_2$ in aqueous solution and undissolved solids consisting of particles (in the micron size range) of sodium aluminosilicate, metal oxides, and residues of the reagent materials. These products are discharged from the digesters (usually through heat exchangers to liberate heat to ingoing mix), put through thickeners (typically with four stages), and finally separated by decantation of the clear sodium aluminate solution from the slurry product. The wastes-solids product is the well-known red mud of the aluminum industry. The red mud is washed with water to remove the final traces of soluble sodium aluminate and recover any residual caustic. The wash waters are recirculated to the beginning of the process and combined with the input to the mixers. From here, the red mud may be moved as a waterborne slurry to a waste area, known as the red-mud lake, and not further processed. In the combination process, applied to high-silica bauxites, the red mud is treated to extract additional amounts of the alumina.

This additional extraction step is accomplished by mixing the red mud with limestone (effectively $CaCO_3$) and sodium carbonate, and the mixture is sintered at 1100 to 1200 C. The important reactions are the conversion of silica to calcium silicate and of the residual alumina to sodium aluminate. The sintered products are leached in a caustic

solution to produce additional sodium aluminate solution which is filtered and added to the main stream operation. The residual solids (brown muds) are slurried to a waste lake.

From either of the alternative processes, purified sodium aluminate solution is passed through heat exchangers and cooled to 50 to 60 C prior to being discharged into large precipitation vessels. By the addition of seed material and by careful control of composition and controlled agitation, alumina trihydrate is precipitated in a controlled form, amenable to easy separation and washing. Precipitation may take 2 to 4 days.

The precipitated trihydrate is dewatered and fed to calcining furnaces. Calcining at 1200 C drives off the excess water, breaks down the trihydrate alumina to simple alumina, and transforms the alumina to a crystalline form (alpha) most suitable for later use in the electrolytic reduction to aluminum metal.

The clarified liquor obtained after precipitation is a mixture of sodium hydroxide and soluble salts of impurities and is reclaimed by processing in multiple-effect, steam-heated evaporators to drive off excess water, bring the NaOH concentration upward toward that desired for reuse, and eliminate the impurity salts. The reclaimed NaOH solution from the evaporators is refortified with new caustic additions and reused in the process.

In general, the purified alumina is transported a considerable distance from the refinery for the smelting or electrolytic reduction to aluminum metal.

The heart of the aluminum plant is the electrolytic cell, or pot, which consists of a steel container lined with refractory brick with an inner liner of carbon. The outside dimensions of the pot may vary from 12 by 15 to 8 by 20 feet or larger. Most cells are around 3 feet in height. The cells are arranged in rows, in an operating unit called a potline, which may contain 100 to 250 cells electrically connected in series. The electrical supply is direct current, on the order of several hundred volts and 60,000 to 100,000 amperes. The carbon liner on the bottom of the furnace is electrically active and constitutes the cathode of the cell when covered with molten aluminum. The anode of the cell is formed of baked carbon blocks supported from above. The electrolyte consists of a mixture of

	Percent
Cryolite	80-85
Calcium fluoride	5-7
Aluminum fluoride	5-7
Alumina	2-8

The fused-salt bath usually is operated at a temperature of 950 C.

Cells presently in use operate with current on the order of 100,000 amperes with a voltage drop across the cell of about 4.5 volts. The reaction in the aluminum reduction cell is not completely understood, but results in the reduction of the aluminum from the apparent Al^{+3} state, assuming ionization in the molten salt, to the Al^{o} state at the carbon cathode at the bottom of the furnace, where the metal collects as electrolysis proceeds. Oxygen, assumed present in the bath as O^{-2}, appears at the carbon anode and immediately reacts with the anode and surrounding constituents to form a mixture of 75 percent carbon dioxide and 25 percent carbon monoxide, which results in the consumption of the carbon anode.

Thus, the operation of the electrolytic aluminum reduction cell results in the continuous consumption of alumina and the carbon anode, and the evolution of gaseous reaction products. The alumina content of the cell is replenished intermittently. The aluminum is withdrawn from the bottom of the molten bath by a vacuum siphon device, at a rate of about 500 to 1800 pounds every 24 hours, although practice may vary. The molten aluminum is collected in ladles and cast into ingots or pigs as the final product of the smelting process.

The continuous consumption of the carbon anode gives rise to the existence of an anode-preparation plant associated with every aluminum plant. The thermal stability and electrical properties of the anodes are of importance to the proper operation of the cell. Two methods of anode preparation are used at present. One method is the prebaked anode practice and the other the continuous anode, or Soderberg process. The anode raw materials are hard pitch and petroleum coke--these are purchased in large quantities to the desired specifications. The preparation of these materials includes crushing and classifying into fractions with particle sizes ranging from 0.2 to 15 mm and blending in carefully controlled proportions. Classifying may be accomplished by various combinations of screens and cyclones handling the different size fractions. The mixtures are preheated to 200 to 300 F to soften the pitch and mixed warm to achieve uniformity of mix and density. This mix is called "anode paste".

In the prebaked anode method, the warm paste is formed into anode blocks in a hydraulic press and the anodes are baked and graphitized by a heating cycle that may, for example, last 15 days with a maximum temperature of 2000 F.

The continuous anode or Soderberg process consists of the continuous supply of anode paste within a consumable aluminum sleeve to the cell. This system relies on the approach of the anode materials to the bath surface to achieve the baking operation immediately before the anode enters the bath.

In either case, the facilities for preparation of anode materials, referred to as the paste plant, include extensive equipment and facilities for dust control and particle classification.

The continuous evolution of the gaseous reaction products from the aluminum-reduction cell yields a large volume of fume which consists chiefly of carbon dioxide and carbon monoxide but also includes significant amounts of volatile fluoride compounds and fine dust evolved from the cryolite, aluminum fluoride, alumina, and carbonaceous materials used in the cell. The removal of this fume from the working area involves extensive air-flow control which may extend to the design of the plant building and hoods, ducts, dust collectors, cyclones, and gas scrubbers. These dust- and air-pollution control measures are the outstanding characteristics of an aluminum plant and account for the major use of water at an aluminum plant.

Water Usage in the Aluminum Industry

Water usage in the primary aluminum industry includes that of the two major divisions of processes in the industry: the alumina refining operations and the aluminum reduction or smelting operations.

The alumina-refining operations (discussed in detail in a prior section of this report) show the major process characteristics of the leaching of the desired Al_2O_3 constituent from bauxite ores by a hot, pressurized, caustic leach with precipitation and drying of the pure Al_2O_3 and the discard of the residue from the original bauxite ore. The general pattern of water usage (Figure 5) includes the uses of water for leaching solution, washing of precipitates and other steps of the chemical extraction process, considerable use for heat-exchange purposes in connection with the control of temperatures in the reaction, i.e., steam heating, flash evaporation, or multiple-effect evaporators, etc. From the viewpoint of water recirculation or discharge, however, the major feature of the water circuit is the red- or brown-mud lakes operated at all alumina refineries. This is analogous to a tailings pond in a flotation concentrator operation, i.e., the mud lake serves as a receiver of solid residues, a receiver and reservoir of process water, a point of evaporation and seepage losses, and a collector of rainfall. It may be noted that water serves as the medium in the transport of the waste portion of the ore to the lake, i.e., some minimum amount of water is required by the mechanics of flushing the material to the disposal plant.

In general, the Bayer process in either of its versions--the standard or the combined process--has no demand for water for use in air-pollution control. The processes used essentially are carried out in closed vessels, with little potential of emissions to the atmosphere. As with any plant, a sanitary water circuit is part of the operation, requiring a source of potable water. Disposal may be to a municipal sewer system, a plant sewer system, or the red-mud lake, with or without any form(s) of treatment.

The general pattern of water use at aluminum smelters would include

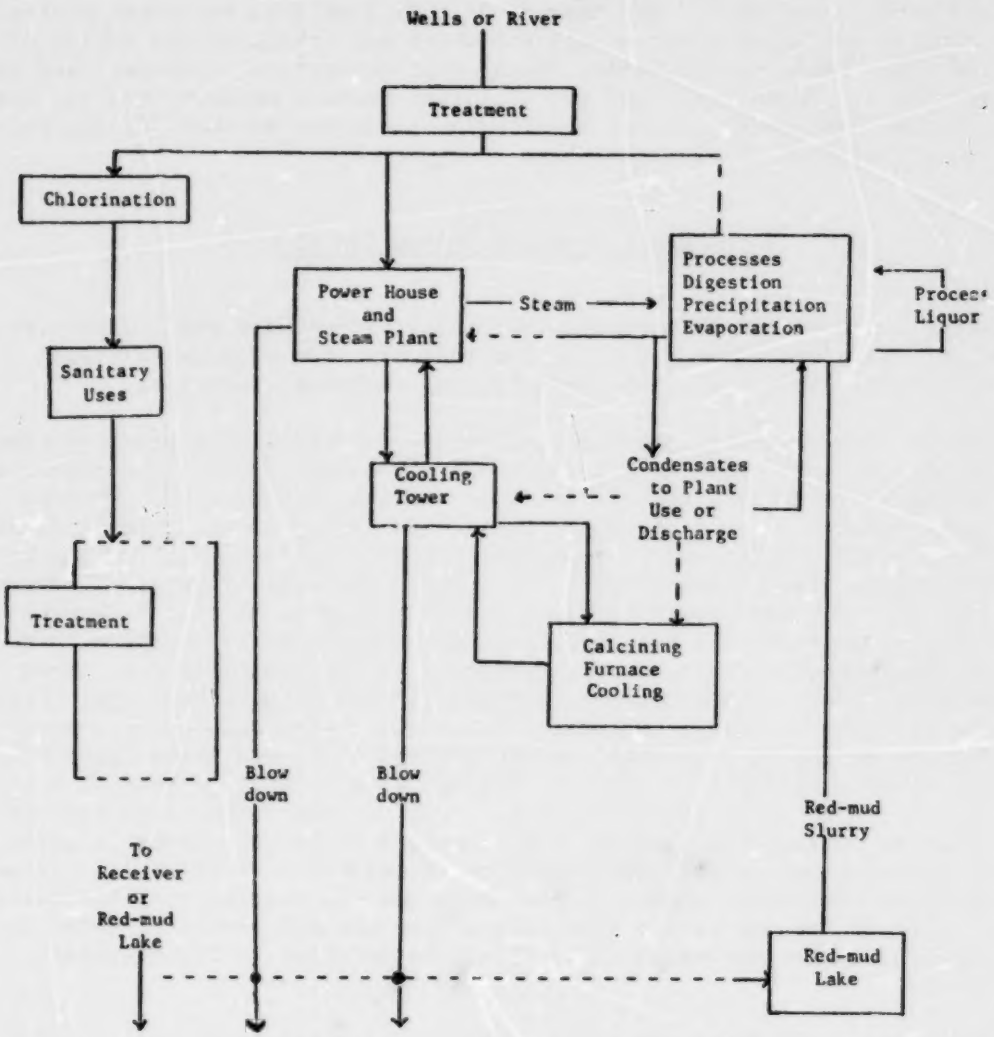

FIGURE 5. GENERALIZED DIAGRAM OF COMMON FEATURES OF WATER CIRCUITS OF ALUMINA REFINERIES

(Figure 6) features of sanitary and boiler uses, and usually cooling circuits applied to d-c power equipment, metal-casting operations, furnace cooling in the anode plant, and miscellaneous equipment cooling. Cooling waters may be recirculated through a cooling tower, used in series or used on a once-through basis, with various discharge practice. The major use of water is in the fume scrubbing operations (if wet systems are used) associated with the anode plant, casting operations, and the aluminum-reduction cells. Here practice varies from once-through methods to a closed circuit with recycle and reclamation.

In the present study, information of varying detail was obtained on 3 alumina refineries with an aggregate capacity of 1.9 million tons of alumina, and on 11 smelters with an aggregate "nominal" capacity of 2.2 million tons of aluminum per year. These data are summarized in Table 6.

The reports on alumina refineries were of two types: generalized reports on groups of plants owned by a single company and specific reports on individual operations. The patterns of water use in alumina refineries showed total plant intakes varying from approximately 10 to 900 million gallons per year with unit intakes ranging from 60 to 1560 gallons per ton of metal.

A breakdown on the distribution of water use within those refineries reporting specific uses was as follows:

	Percent
Cooling	77.3
Sanitary	11.1
Process	9.4
Other	2.2
	100.0

Process uses include both direct addition to the process stream or makeup water to the red mud lake, which may be used in either process or other uses, depending on recirculation. The breakdown shows no use of intake for boiler feed, as this is derived from process condensates.

The "other" category includes uses such as treatment of incoming water, uses in instruments, and numerous small uses about the plants. The plants all show high recirculation rates, where such ratios could be defined, i.e., the ratios of actual flows to intakes of new water were 8.6 for process water and 15.6 for cooling, while boiler feed and some cooling water supply was being derived from process condensates. Total consumption ranged from 60 to 259 gallons of water per ton of alumina produced, i.e., 0.03 to 0.12 gallon per pound.

Discharges ranged from 0 to 1,370 gallons per ton of alumina, with the minimum intake corresponding to minimum consumption, i.e., 60 gallons per ton for both values, and these were associated with zero discharge.

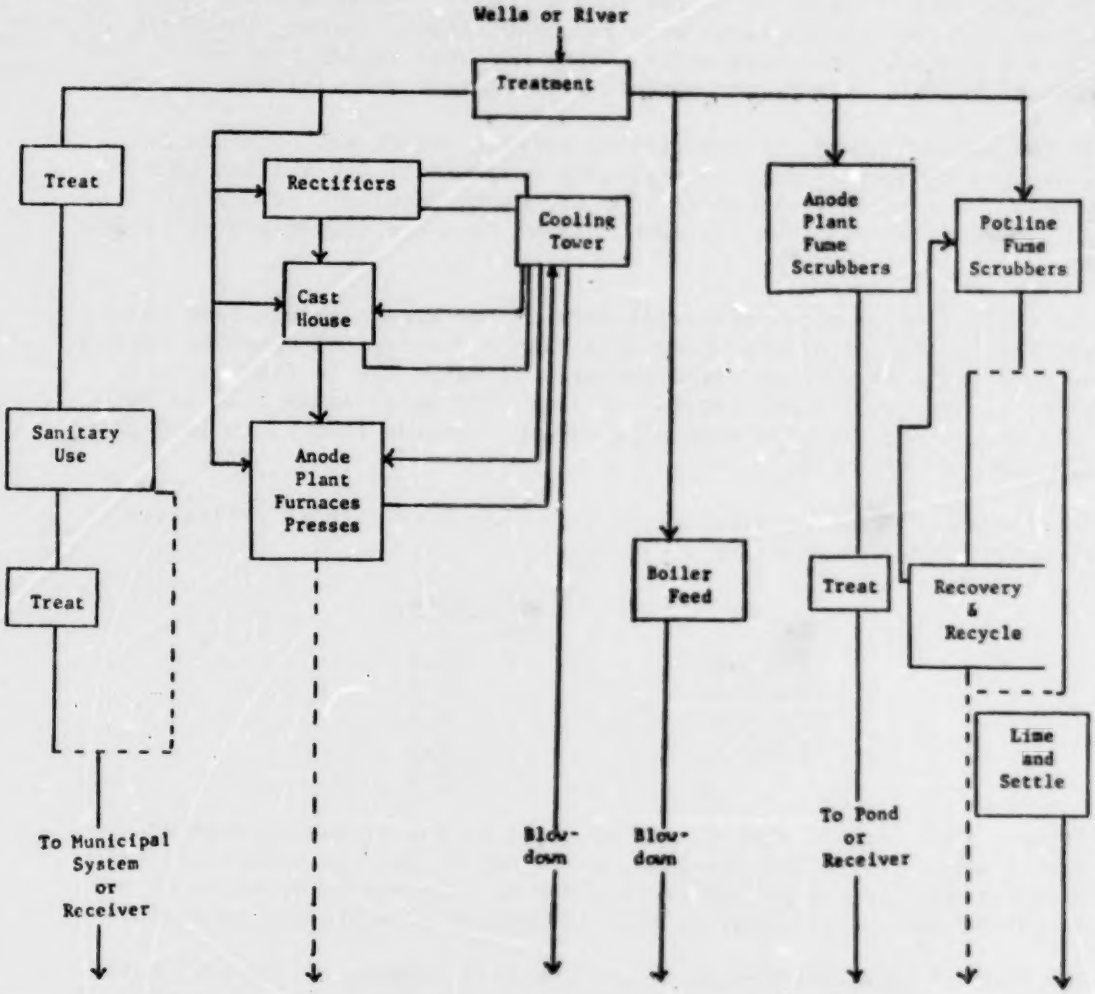

FIGURE 6. GENERALIZED DIAGRAM OF COMMON FEATURES OF WATER CIRCUITS OF ALUMINUM SMELTERS

The pattern of water use at aluminum smelters is indicated by the data in Tables 6 and 7. Here plant intakes are shown to vary from 89 to 7,000 million gallons per year, with the plant with lowest total intake showing greatest unit intake, again reflecting the range of variations in individual plants.

The two most significant factors in water use and discharge pattern have been related to the scrubbing of potroom fumes. The approaches to this have varied over the years to include

1. No scrubbing

2. Wet scrubbing using once-through water (discharged with or without treatment)

3. Wet scrubbing with recirculation of water and reclamation of contained fluorides, alumina, etc.

4. The use of dry scrubbing systems, using no water, which allow reclamation of fume components.

Current economic and other pressures have brought almost all the industry to States (3) and (4). The dry fume-scrubbing method is being installed in some of the plants currently under construction, and has been or is being installed to replace wet scrubbers in some of the older plants. The dry fume-scrubbing system reduces plant water requirements to sanitary, boiler feed, and heating needs. Thus, the potential exists for the elimination of air pollution, a large decrease (i.e., ≥ 75 percent) of water intake, the elimination of all discharges of process-contaminated waste water, and the reclamation and recycle of formerly wasted materials. This classic engineering feat is currently the property of the originating company, but its potential spread through industry makes predictions of future water usage largely useless, as the presence or absence of this system changes the water use at any plant almost by the entire amount of water which would be predicted for any other system.

Nevertheless, some aluminum-smelting plants will probably continue to exhibit the variegated water usage and discharge patterns indicated in Table 7.

These patterns are determined by the interrelationships of water costs, local water availability, individual plant design, and climate.

Waste-Water Characteristics and Amounts

Alumina Refineries

The waste-water characteristics associated with alumina refineries

TABLE 6. WATER DATA FOR ALUMINA REFINERIES AND ALUMINUM SMELTERS

Total Water Intake, MGY	Discharge to Receiving Waters, MGY	Total Use, New and Recirculated, MGY	Water Intake per Ton of Metal[a], gal	Water Used per Ton of Metal, gal	Consumption (Intake minus Discharge), per Ton of Metal, gal
		Alumina Refineries			
57.1	0	--	60	--	60
10.2	0	--	60	--	60
907	756	--	1,560	--	259
		Aluminum Smelters			
89[b]	0	--	104,500	--	104,500
1,462	617	--	6,090	6,090	3,520
7,000	7,000	7,000	48,600	48,600	0
4,900	4,620	101,400	19,600	406,000	1,120

(a) Per ton of Al_2O_3 for alumina refineries.

(b) Represents a number of smelters operated by a single company

TABLE 7. WATER USES AND RECIRCULATION PRACTICE IN ALUMINUM SMELTERS

Percent of New Water Intake						Use Rate Ratio by Process						
Process	Cooling	Boiler Feed	Air Pollution Control	Sanitary	Other	Process	Cooling	Boiler Feed	Air Pollution Control	Sanitary	Other	Overall
5.4	50.9	1.7	24.8	17.2	--	--	--	Recirculation Used			--	--
--	29.5	--	70.0	0.5	--	--	--	None	--	--	--	--
--	28.5	--	66.0	5.4	--	--	1.8	--	28.9	1	--	19.7

have previously been labeled "not a pollution problem". However, these waste waters or their components as found by this survey were reviewed because they contain components or impurities common to many industrial plant operations. The specific components of the total waste water may include

Sanitary wastes
Cooling water
Intake water treatment plant effluents
Pump bearing cooling
Boiler blowdown
Demineralizer resin regeneration waste water.

The reported compositions of such waters are given in Table 8. It may be seen that none of these waste waters reflect the characteristics of the process, i.e., a hot caustic leach. The number of analyses related to intake water treatment is occasioned by the fact that some alumina refineries are located on the lower reaches of rivers and use them as sources. The waste waters from intake water treatments include:

1. A sludge containing $Fe(OH)_3$ and $CaSO_4$ which is flushed away using enough river water to transport the solids

2. The stream from the neutralization of the regenerating reagents used on a resin demineralizer.

In the latter case, NaOH and H_2SO_4 solutions are used to regenerate the resin and are then combined to neutralize each other, the supernatant (i.e., the given analysis) is waste to receiving waters, and the settled sludge is otherwise disposed of.

Two other examples of common industrial-waste-water types are given in Table 8. The analysis of cooling-tower water shows relatively high values of total hardness, dissolved solids, and chlorides, and the presence of chromates used to inhibit corrosion of and deposits on tubes and pipes. The composition of boiler blowdown also is shown in terms of its major constituents, phosphates and sulfites. These also originate from chemicals added to prevent corrosion and caking.

Aluminum Smelters

A thorough study of aluminum-smelter waste waters has been published as the result of a program connected with the planning, design, construction, and initial operation of a new plant using a wet-scrubber system located on the northwestern coast of the United States.[12] The program included the early determination of effluent characteristics using samples from existing plants, preoperation surveys of the environmental conditions in the planned area of discharge, studies of the interaction of effluent samples with the receiving seawater, and monitoring of the

TABLE 8. WATER ANALYSES, PPM, ASSOCIATED WITH ALUMINA-REFINERY OPERATIONS

	Intake	Waste Water	Cooling Tower	Sanitary Wastes[a]	Intake Water Treatment Sludge	Boilers Blowdown	Resin Bed[b] Regenerating Waste Water
"P" Alkalinity as $CaCO_3$	0	17.	0	--	--	--	--
"M" Alkalinity as $CaCO_3$	96.	24.	21.	--	--	--	--
"O" Alkalinity as $CaCO_3$	0	10.	0	--	--	--	--
Carbonates	0	14.	0	--	--	--	--
Bicarbonates	96.	0.	21.	--	--	--	--
Total Hardness	120.	75.	390.	--	--	--	--
Total Dissolved Solids as NaCl	175.	140.	737.	--	--	--	--
Silica	10.	8.	--	--	--	--	--
Chromate as CrO_4	--	--	44.	--	--	--	--
Chlorides as Cl	24.	21.	110.	--	--	--	--
BOD	--	--	--	10-30	--	--	--
pH	7.1	9.8	6.5	--	--	--	--
$Fe(OH)_3$	--	--	--	--	220	--	--
$CaSO_4$	--	--	--	--	2400	--	--
PO_4	--	--	--	--	--	20.	--
SO_3	--	--	--	--	--	13.	--
Total Solids	--	--	--	--	--	400.	--
Na_2SO_4	--	--	--	--	--	--	3460.

(a) After treatment
(b) Discharge is intermittant; regenerating agents are NaOH and H_2SO_4.

conditions around the discharge point after plant start-up.

The published results of the study included the listing of characteristics of samples of smelter waste waters, shown in Table 9. Studies of the settling characteristics in seawater of the materials contained in the waste water proved that the coarser fractions of particulates settled while the finer particles rose to the surface. These and other studies showed that the effluent would be dispersed so effectively from its point of outfall (1800 feet offshore) that no effect on the environment was expected.

Examples of water analyses reported by aluminum-smelter operators during this study are given in Table 10. Anode plant scrubber waters were characterized as being contaminated with tars, oxides of carbon and sulfur, and hydrofluoric acid, as indicated in the table. In the plant reporting this analysis, these waters are settled and skimmed to remove solids and oils, and diluted with cooling water before release.

TABLE 10. WATER ANALYSES, PPM, ASSOCIATED WITH ALUMINUM-SMELTING OPERATIONS

	Anode Plant Scrubber Water	Potline Scrubber Waters			Cast[a] House Discharge	Treated Sanitary Wastes
pH	3.4-3.6	3.0-3.1	4	--	8.2	7.0
SO_4	20-30	--	--	--	230.	--
F^-	13-23	120-150	30-50	50-90	--	0
Oils	4-14	--	--	--	--	--
S[b]	70-150	200-500	30	--	--	<30
Hardness	--	--	--	--	230.	--
Chlorides	--	--	--	--	70.	--
BOD	--	--	--	--	--	50-62

(a) Treated with commercial additives to allow recirculation.
(b) Suspended solids.

The potline scrubber waters exampled show the characteristic influence of HF fumes: low pH and fluoride-ion content varying from 50 to 150 ppm, with some variation in suspended-solids contents. These particular waters were variously recycled or discharged without treatment.

The example of cast house cooling water exhibits characteristics due to additions of a commercial additive permitting recirculation and reuse before discharge, while the analysis of sanitary wastes shows characteristics of treatment in a system referred to as a "package plant".

TABLE 9. PUBLISHED DATA ON ALUMINUM SMELTER WASTE WATERS[12]

	Plant A			Plant B		
	Minimum	Maximum	Average	Minimum	Maximum	Average
Total Residue, ppm	407	540	464	356	361	358
Filterable Residue, ppm	332	487	420	193	236	214
Nonfilterable Residue, ppm	16	75	44	125	163	144
Total Aluminum, ppm	0.8	22	9.8	7.8	26	14.5
Fluoride, ppm	--	--	145	93	116	107
pH	3.6	4.0	3.8	2.9	3.2	3.1
Chloroform and Ether Extractables, ppm	--	--	--	--	--	22.9

The information supplied concerning water quality during use in the fume-scrubbing operation indicated that scrubber water immediately after use will contain up to 1/2 percent hydrofluoric acid, but that this level must be reduced to permit recirculation, i.e., the vapor pressure of the dissolved HF markedly affects the collector efficiency.

A prior (1952) study of water requirements, use, and disposal in the aluminum industry dealt with the then existing six alumina refineries.(10) In this prior study, the following uses of water were listed for alumina refineries:

	Intake per Day, thousands of gallons	Percent of Total Intake	Intake per Year(a), millions of gallons
Sanitary and washhouse	984	8.4	344.4
Cooling water	3,591	30.4	1,256.9
Hydrate wash	550	4.7	192.5
Red-mud-lake makeup	6,676	56.5	2,336.6
Total	11,801	100.0	4,130.4

(a) Assuming 350 operating days per year.

A ratio of water intake to product of 0.66 gallon per pound of alumina (or 1320 gallons per ton) was reported. However, the variation among individual plants ranged from 0.28 gallon to 1.10 gallons per pound of alumina. Moreover, at that time, a modification was planned at one plant which would increase the average water intake from 0.66 to 3.48 gallons per pound of alumina and widen the range for individual plants to 0.28 to 26.0 gallons per pound.

The same prior study included water use at 14 aluminum smelters and gave the following breakdown of uses:

	Intake per Day, thousands of gallons	Percent of Total Intake	Intake per Year(a), millions of gallons
Engine cooling	1,168	1.1	408.8
Compressor cooling	714	0.7	249.9
Sanitary	8,682	8.3	3,038.7
Boiler feed	416	0.4	145.6
Electrode plant	1,420	1.4	497.
Rectifiers and transformers	13,524	13.0	4,733.4
Gas scrubbers	78,599	75.1	27,509.7
Metal-casting cooling	1,357	1.3	475.0
Total	104,523	100.0	36,583.18

(a) Assuming 350 operating days per year.

The data show that the largest single use of water by the smelters was for gas scrubbing (75 percent). The average water use for the entire industry at that time was given as 14.62 gallons per pound or 29,240 gallons per ton of aluminum. Again, intake varied widely for individual plants, from 1.24 to 36.33 gallons per pound of aluminum.

The treatment and disposal practices at the time of the prior survey are reported in Table 11. The alumina plants showed a strong emphasis on recirculation, with two-thirds of the refineries recirculating process water and one-third discharging to a river. On the other hand, waste-water-disposal practices at the smelters were divided between discharging the process water and recirculating it.

TABLE 11. PAST WASTE-WATER-TREATMENT PRACTICE IN THE PRIMARY ALUMINUM INDUSTRY(10)

Treated	Receiver	Type of Waste Water	
		Sanitary	Process
	Alumina Refineries (6 Plants)		
Yes	Red-mud lake	1	0
Yes	Stream	1	0
No	Red-mud lake	2	4
No	Stream	1	2
No	Estuary	1	0
	Aluminum Smelters (14 Plants)		
Yes	Stream	8	1
Yes	Estuary	2	1
Yes	Septic tank	1	0
	Recirculated	0	5
No	Stream	3	7

Note: Numbers indicate number of plants using indicated practice.

The discharges of waste water from alumina refineries were characterized as involving no pollution problems. These discharges consisted chiefly of cooling water, cooling-tower blowdown, or condensate from the evaporator after-condenser in the processing sequence.

The waste waters discharged by the smelters were characterized as being acid by virtue of their fluoride content. The two (of fourteen) plants then treating water before discharge were using a practice of liming in settling ponds, with the sludge disposed of in landfill.

The data from the 1952 survey may be compared with the data obtained in this survey in the following terms:

	1952	1970
Number of Refineries Surveyed	6	3
Gallons Intake per Ton of Al_2O_3 Product	560-2,200	60-1,560
Number of Plants With Untreated Discharge	2	0
Number of Smelters Surveyed	14	11
Gallons Intake per Ton of Aluminum Product	2,480-72,660	6,090-104,500
Number of Plants With Untreated Discharge	7	1

The apparent changes are decreased water intake with better control of discharges at alumina refineries, and increased intake and increased control of discharges at aluminum smelters.

Water Costs

The water costs were reported in various terms and showed a wide range in terms of costs, designs, practices, and treatments. The terms and items reported were reduced to common terms of capital investment and running (operating and maintenance) costs in terms of capacity of the individual water operation. The results are given in Table 12. Total water costs varied from less than 1 to 10 cents per thousand gallons for the three plants reporting in these terms. Of the various water treatments reported, the standard treatments, i.e., chlorination, sewerage treatment, and boiler feed (chemical softening), fell in the usual brackets of costs assignable to them. The cooling-tower operation reported served a smelter circuit including rectifiers and cast house cooling functions with water treated for recirculation. The anode-plant fume-scrubber water treatment reported consisted of settling and skimming operations to remove, respectively, suspended solids (75 percent removal) and oils (80 percent removal). One plant reported potline scrubber water treatment with reclamation of contained materials and recycle of the water, which could be related only to total production, as costing $0.26 per ton of aluminum produced. The only other cost information supplied was that a change in a potline scrubber water circuit from once-through to reclaim and recycle was expected to cost about 1.4 million dollars and would treat an estimated 16 billion gallons per year in the recirculating system. On the basis of the data reported, total water costs were calculated to be on the order of 0.05 to 0.1 percent of the product value, using a value of $0.30 per pound of aluminum. However, none of the operators included all costs such as depreciation, etc., in their reports.

TABLE 12. WATER COSTS IN THE ALUMINUM INDUSTRY

Category or Operation	Capital Investment, $/1000 gal/yr capacity	Operating and Maintenance Costs, $/1000 gal
Total plant water	1.32	0.074
Ditto	1.27	0.10
"	--	0.0065
Intake system	2.46	0.07
Ditto	0.50	0.04
Sewerage treatment	2.43	0.54
Boiler feed treatment	0.34	0.35
Chlorination	0.04	0.01
Cooling tower	0.25	0.007
Anode-plant fume-scrubber water treatment	0.07	0.008

Waste-Water-Treatment Practices, Plans, and Needs

For the three refineries and eleven smelters contributing information to this study, current waste-water treatment practices were identified as:

Two Refineries	Zero discharge
One Refinery	Discharges consisting of treated sewerage and untreated cooling water.

Of the total of 2.2 million tons of smelter capacity surveyed here, the breakdown of fume-treatment practice was as follows:

	Aluminum Production Capacity, percent
Dry fume scrubbing	22
Wet fume scrubbing with recycle	60
Wet fume scrubbing water treated	6-1/2
Water partially treated	11-1/2

In the first category, no "process" water would be discharged: discharges would thus consist of sanitary, cooling waste waters, and minor amounts of boiler blowdown. The last group included two plants, one of which treated anode plant scrubber water but not that from potline scrubbers. Both the latter plants currently are planning to convert to

recycling systems to reduce water requirements and discharges.

With these plans announced by the responding plants and indications from announcements in current journals, it would appear that almost all existing smelters will be refitted, and all new construction will use either the recycle system of wet scrubbing or the new dry fume-scrubbing system. Thus water intakes and discharges by the industry will follow a new and greatly reduced rate of increase relative to expansion of production capacity.

The only problem expressed by two respondents was the need for better ways to remove or recover fluoride ions from waters also containing sodium, aluminum, and sulfate ions. This need is applicable to both the recovery system which is considered adequate now but not completely efficient, and the treatment of the necessary small bleed-off of some recovery systems.

SECTION VI

THE PRIMARY MERCURY INDUSTRY

Size and Characteristics of the Industry

The current (1971) conditions in the mercury industry preclude anything but a historical treatment of mercury production and operations. Under the effects of a number of factors affecting price, consumption, and operation, the mercury industry is in the midst of a drastic slowdown. The domestic production for 1970 may be estimated at about 28,000 flasks, while that predicted for 1971--on the basis of first-quarter production (4,488 flasks)--may be 18,000 flasks.

The latest year for which complete statistics have been published is 1969.[13] In 1969, 109 mines produced 29,860 flasks of primary mercury. The major producing mines for that year are listed in Table 13 and their locations are shown in Figure 7. Mines in California and Nevada produced 26,645 flasks (91 percent of the total) and the balance was produced by mines in Idaho, Alaska, Arizona, Texas, and Oregon.

The major uses of mercury are indicated by the 1969 consumption pattern published by the Bureau of Mines. These are listed in Table 14 in order of decreasing amounts. The difference in the figures for production and consumption is due to imports and government stockpile inputs. However, this list is of only historical interest, as the consumption of chloralkali plants (for amalgam electrodes) and by agriculture (for pesticides) is rapidly changing because of efforts to curtail mercury emissions to the environment.

The primary mercury consumption shown in Table 14 is supplemented by products known as redistilled and secondary mercury, so that total consumption of all three forms amounted to 79,104 flasks (a flask is equal to 76 pounds of mercury).

Raw Materials and Processes

Although there are 25 known mercury-bearing minerals, the primary source of this metal is cinnabar (mercury sulfide). Other economically important mineralogical species of mercury include native metallic minerals of iron, arsenic, and antimony.

The gangue associated with cinnabar deposits includes carbonate and silicate minerals such as calcite, chalcedony, dolomite, opalite, quartz, and serpentine. The deposits usually are shallow, extending downward to

TABLE 13. MERCURY-PRODUCING MINES IN THE UNITED STATES IN 1969[13]

State	Production Categories		
	1000 Flasks or More	500 to 1000 Flasks	100 to 500 Flasks
California	Buena Vista Gambonini Gibraltar	Abbott Culver-Baer	Altoona Chileno Valley Corona El Capital Juniper Klau Knoxville New Almaden Oat Hill Petray
Nevada	B&B Quinn River Runa	Goldbank	Cahill Horton's Mercury
Idaho	Idaho-Almaden		
Texas	Brewster		
Alaska			Cinnabar Creek White Mountain

TABLE 14. FORMS AND AMOUNTS OF CONSUMPTION OF PRIMARY MERCURY[13]

Consumer	Number of Flasks
Chloralkali plants	19,263
Electrical apparatus	13,260
Paint	9,730
Miscellaneous	8,427
Instruments	2,832
Agriculture	2,689
Catalysts	2,235
Laboratory use	1,232
Pulp and paper making	558
Pharmaceuticals	360
Dental preparations	214
Amalgamation	194
Unknown	134
Total	61,128

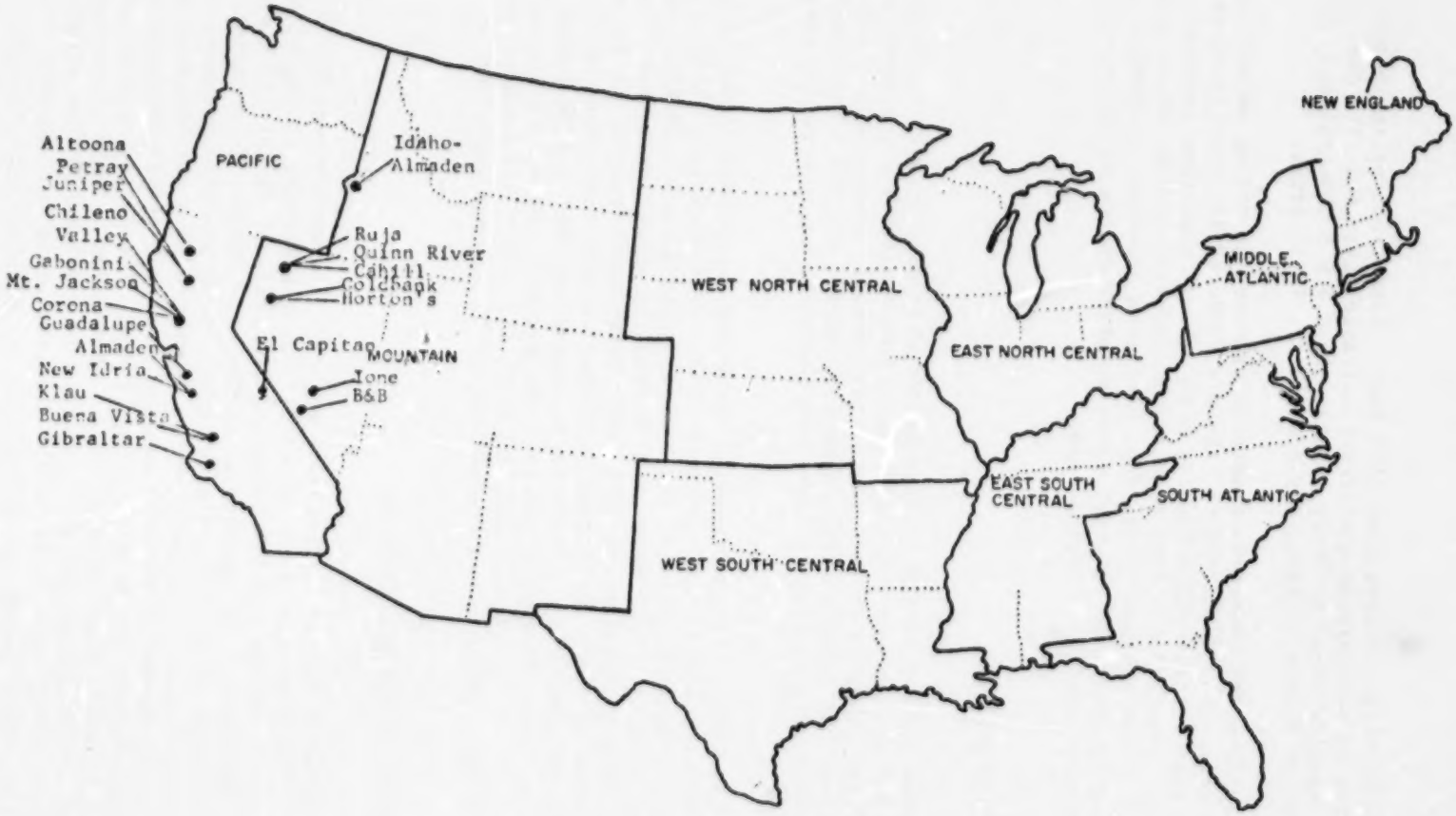

FIGURE 7. LOCATIONS OF MERCURY MINES

depths of slightly less than 2500 feet. Almost all of the deposits are in areas of tertiary or quaternary volcanic activity. The most important deposits occur in Italy, Spain, the U.S.S.R., Yugoslavia, China, the United States, Canada, Mexico, and the Philippines.

Both surface and underground methods are used in mining mercury ore. To be economically attractive, the ore produced in underground operations must contain significantly more mercury than that produced in open-pit operations. Ores produced in open-pit mining, which contain 2 to 3 pounds of mercury per ton, have been processed economically. Mercury contents two to three times greater are needed for economically attractive underground operations.

Ore Preparation

The mine-run ore is transported to the crusher bins from which it is conveyed to a screen where the minus-3-inch material is removed and the oversized fraction is reduced to about minus 3 inches with a jaw crusher. Both the undersized material from this screen and the crushed ore then are conveyed to a fine-ore bin from which the raw ore is fed into the furnace.

Conventionally, the mined ore is subjected to pyrometallurgical treatment without preliminary concentration. On the basis of differences in the physical properties of the mineral species, e.g., density, methods of concentration have been used in specific instances. These include hand, rotary, jigging, tabling, and flotation. The last is the most effective of these techniques, yielding mercury recoveries of approximately 90 percent and concentrates containing 500 to 1000 pounds of mercury per ton. Flotation necessitates grinding the ore to the relatively fine size of the concentrate, however, and yields a feed more amenable to retorting than to continuous mechanical furnace operation.

Pyrometallurgical Processing

The pyrometallurgical processing of mercury ores involves heating the ore in the presence of air to volatilize the mercury in the elemental form. All of the current domestic production of mercury is based on this technique. The mercury vapor from the furnace is condensed and treated with lime to produce relatively pure metallic mercury. The pyrometallurgical treatment may be conducted in a batchwise manner in indirectly heated retorts or in continuous mechanical furnaces such as multiple-hearth roasters or rotary kilns. The latter type of mechanical furnace is most commonly used in the larger plants currently operating in the United States. Figure 8 is a schematic flow diagram of a typical rotary-kiln installation for processing mercury ore. In the process, the crushed ore is fed into the kiln against a countercurrent

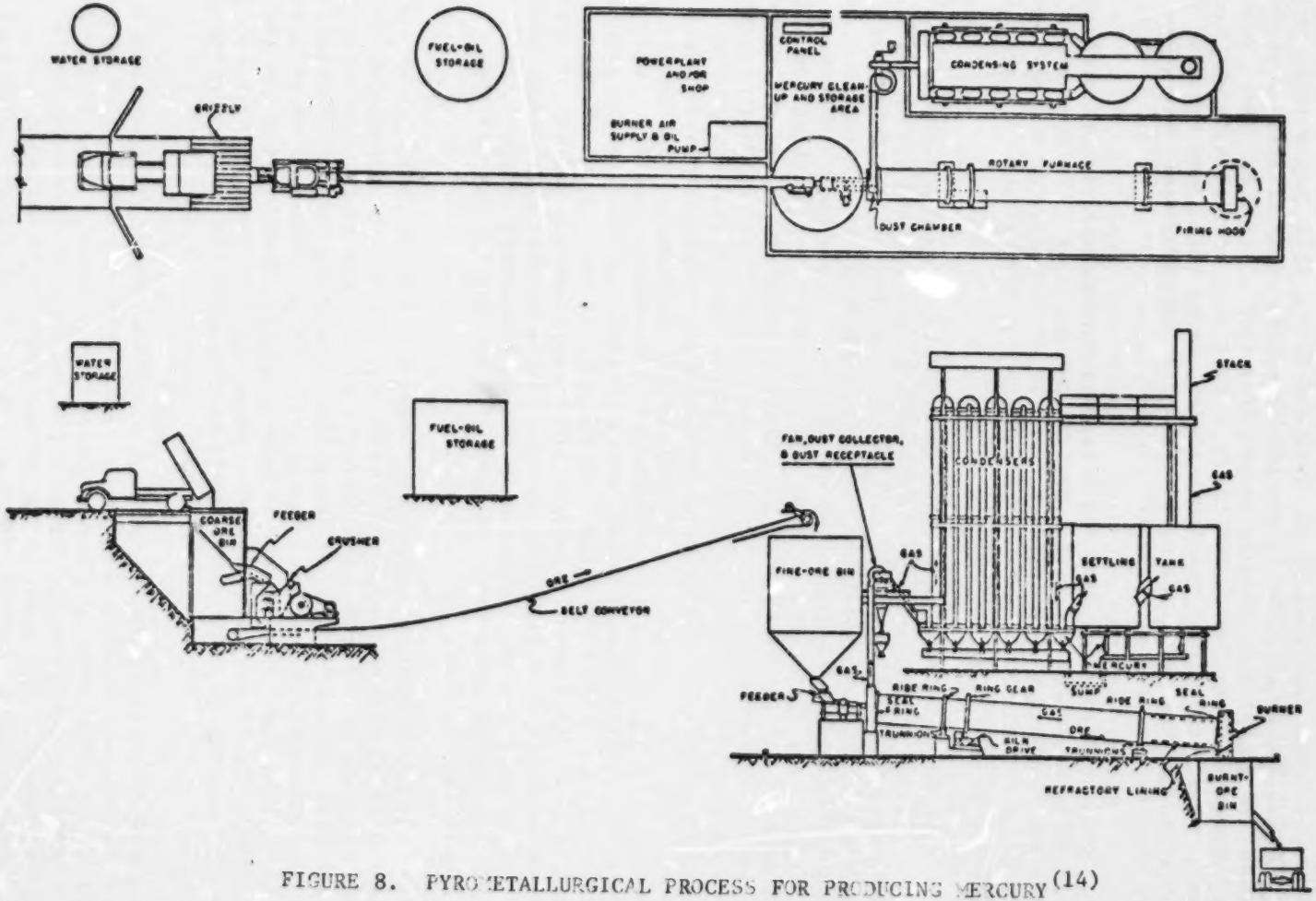

FIGURE 8. PYROMETALLURGICAL PROCESS FOR PRODUCING MERCURY (14)

flow of hot combustion gases with a shotgun feeder. The temperature of the gases being exhausted at the feed end of the kiln ranges from 600 to 650 F. The temperature of the barren solids being discharged at the firing end of the kiln usually ranges from 1000 to 1500 F. These solids may be cooled to as low as 200 to 300 F by direct contact with the incoming air, either in an auxiliary cooler, or as they leave the discharge end of the kiln. To avoid leakage of mercury vapor, the kilns are operated at less than atmospheric pressure.

The mercury-laden gases from the kiln pass through one or more cyclone separators to remove the finely divided particulates. The dust collectors are operated at 450 to 500 F to avoid condensation of the mercury vapor. The dust products from the cyclone and the calcined ore are transported to the waste-disposal area.

After the mercury-laden gases pass through the cyclone and the hot fan which follows, they usually are divided into two streams and injected into two banks of air-cooled, vertical U-tube condensers. These condensers are about 16 inches in diameter and from 20 to 40 feet in height. The individual pipes are connected at their tops and bottoms with U-turns. At the bottom these U-turns have openings which are sealed with water through which the condensed mercury flows and is recovered. The condensers are constructed of cast iron, mild steel, tile, stainless steel, or Monel, depending largely upon the sulfur and/or chloride content of the ore and the subsequent corrosiveness of the gases. The total length of the condenser depends on the tonnage of material being processed in a particular kiln and the resultant flow of combustion gases. The condenser system normally is designed to provide a temperature of less than 110 F at the exhaust end. Although the condensers normally depend on natural air circulation for cooling, it is common practice to spray water on the outside of the hottest pipes in the condensing system, particularly during the summer months. The major portion of the mercury condenses in the initial four or five pipes in the condenser.

After the gases leave the condenser, they are expanded into one or two large baffled redwood tanks for further cooling and the subsequent removal of some of the remaining mercury. From these tanks, the waste gases pass into the bottom of the stack, from which they are emitted into the atmosphere at temperatures of 60 to 90 F. Sometimes water is sprayed into the bottom of the redwood expansion chambers and the stack to effect additional cooling of the gases prior to their release into the atmosphere, in order to decrease mercury emissions and to increase yield.

The metallic mercury, dust, and soot collected in the condenser system are removed periodically and transported to either a manual or a mechanical hoe table where the impure product is mixed with lime to recover the mercury. During this operation, the mercury coalesces and flows into a sump at a low point in the table, where it is collected and bottled in flasks. The residue from the hot table either is returned

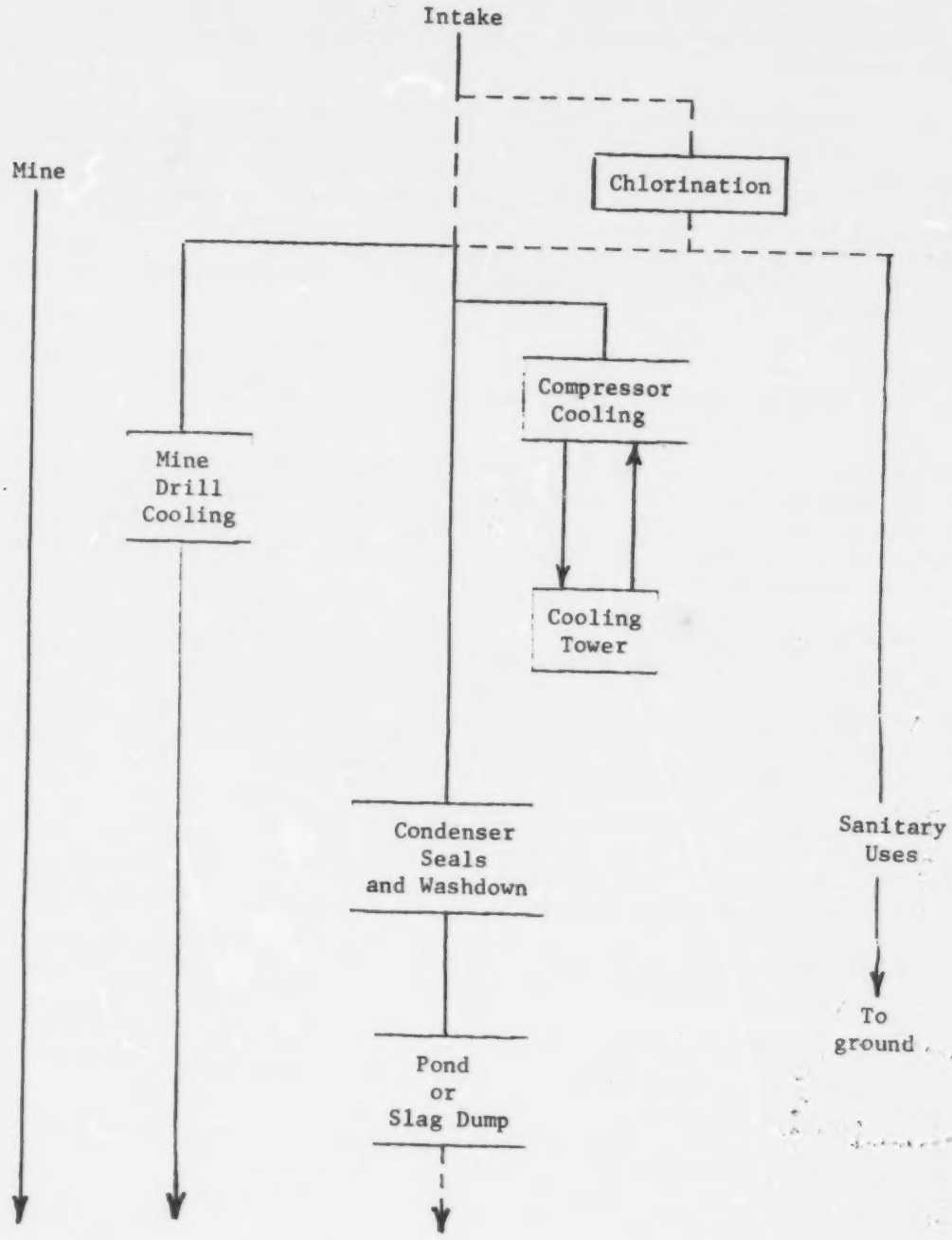

FIGURE 9. GENERALIZED DIAGRAM OF COMMON FEATURES OF WATER CIRCUITS OF MERCURY MINES AND PLANTS

to the rotary kiln for processing or is mixed with other mercury-containing materials and processed in an indirect-fired retort in order to increase yield.

In some mercury-producing operations involving the processing of relatively small tonnages of raw materials--either raw ore or concentrates--retorts may be used as the primary processing furnaces. Since the retort is an indirectly fired unit, the volume of mercury-laden gases is much less than that produced in a direct-fired rotary kiln. This diminished volume of exhaust gases decreases the overall loss of mercury to the atmosphere and improves the mercury recovery efficiency by a few percent.

Water-Usage Patterns, Practices, and Problems

Representatives of three mercury-producing companies responded to this survey program. Responses were sparse because of numerous closings and current pressures on more salient problems. However, most mercury furnacing operations are similar and these few responses will be discussed for the insight which they contain.

The water-usage patterns reported contained the elements indicated in Figure 9. The only process-type water consists of the water pool which forms the seals at the bottoms of the condenser U-tubes, and any wash water used in periodic cleaning of the inside of the condenser tubes for maintenance purposes. One instance was reported of the use of a closed-circuit cooling system for associated air compressors.

Remote locations and an arid climate are characteristics of most of the mercury operations. Thus, one mine operation reported the use of bottled drinking water and chemical toilets, but did have a discharge of mine water. No furnacing operation was associated with this mine.

The three operations had capacities to mine and process about 200,000 tons of ore a year and showed the following discharges of water.

Intake, MGY	Discharge, MGY	Type of Discharge or Receiver
5	0	Evaporation pond
250	250	Untreated; to surface water
60	46	Mixed mine and process water

In the last example, waste waters were percolated through the slag or tailings dump and the effluent from the heap was diluted with fresh water. The diluted effluent which constituted the discharge to the receiving water had the following analysis:

	mg/l
Nitrate	2.4
Chloride	63.8
Sulfate	2382.6
Bicarbonate	12.2
Carbonate	0
Sodium	186
Potassium	23.0
Calcium	289.6
Magnesium	294.4
Fluorides	1.7
Silica	18.0
Iron	0.02
Manganese	2.4
Boron	3.7
Cyanide	0.03
Lead	0.000
Arsenic	0.000
Copper	0.08
Mercury	0.02
Total Hardness	1950.0
pH	4.8-5.7

Considerable elevation of the contents of dissolved salts and some metals are apparent in this analysis.

The information obtained on the primary mercury industry is so scant as to serve only as an isolated example. However, even among the various aspects of the present state of the industry, there is the long-range possibility of one process modification to overcome the problem of mercury emissions to the atmosphere which would affect water usage by the industry. One of the possible alternatives to the present processes is hydrometallurgical processing.

Potential Hydrometallurgical Processes

Over 90 years ago, Volhard reported that an aqueous solution of sodium sulfide can be used for dissolving cinnabar. Until recently, however, the only hydrometallurgical technique used was developed in 1915, for the recovery of mercury from amalgamation. In the late 1950's the U.S. Bureau of Mines conducted considerable research on the use of sodium sulfide and sodium sulfide-sodium hydroxide solution for leaching mercury ores and concentrates.(15-17)

The great variations in composition of ores, the cost of grinding ores finely enough for effective leaching, the simplicity and efficiency of pyrometallurgical processing, and the cost of reagents generally have

precluded the consideration of hydrometallurgical processes for the recovery of mercury. However, if flotation is used to concentrate the ore, the cost of alkaline sulfide leaching followed by electrolytic precipitation of the mercury has been estimated to be about the same as the cost of pyrometallurgical treatment. This leaching-electrolytic technique has been evaluated at least to the pilot scale at the Hermes plant in Idaho.[14]

Other hydrometallurgical processes which have been developed for the recovery of mercury include hypochlorite leaching and electrolytic oxidation.

In 1964, U.S. Bureau of Mines investigators[18] estimated the costs involved in the mining and hydrometallurgical treatment of ores from both open-pit and underground mining operations. The grade of the ore from the open-pit operations was assumed to be 4 pounds of mercury per ton; that from the underground mining was assumed to be 20 pounds of mercury per ton. At ore-treatment levels of 250 tons per day for the lower grade and 50 tons per day for the higher grade, the treatment costs were estimated to be $5.29 and $33.33 per ton, respectively. Costs for mining and treating the ores from open-pit and underground mining operations by conventional pyrometallurgical techniques were estimated to be $3.95 and $33.10 per ton, respectively.

The literature indicates that

1. Hydrometallurgical processes for treating mercury ores have been developed--at least to the pilot-plant scale

2. Estimated costs of treating some mercury ores by hydrometallurgical and pyrometallurgical techniques are similar.

Nevertheless, the literature does not indicate any extensive utilization of hydrometallurgy for recovering mercury from domestic ores or concentrates. This may be due to the relative simplicity of both processing and processing equipment involved in the pyrometallurgical technique.

Treatment of finely ground ore through flotation and chemical processing should not lead to significant emissions of mercury to the atmosphere. However, it is probable that soluble mercury compounds would be left in the tailings from the leaching operations, even with careful countercurrent washing. This would create a water-pollution problem which might require considerable effort to eliminate.

Since no data are available on the potential losses of mercury in the solid residues and waste waters from sizable hydrometallurgical operations, it would be very difficult to estimate either the magnitude of the water-pollution problem or the cost of alleviating it. Lack of such information precludes further consideration of hydrometallurgical processing as a possible means of air-pollution control at this time.

If further consideration is believed desirable, old records from previous research and development on this technique should be reviewed to acquire information specific to the water-pollution potential of this technique.

SECTION VII

THE PRIMARY GOLD AND SILVER INDUSTRIES

Size and Characteristics of the Gold Industry

In 1969, the United States gold industry produced about 1.7 million ounces of gold from sources of ore shown in the following tabulation:(19)

	Gold Ore, short tons	Gold Recovered, troy ounces
Placer Mines	--	25,418
Gold Mines	3,392,503	1,031,050
Gold-Silver Mines	208,105	1,883
Silver Mines	654,674	2,900
Copper Mines	189,279,503	579,171
Lead Mines	369,355	3,069
Zinc Mines	760,057	1,057
Copper-Lead-Zinc, etc. Mines	3,725,190	84,742
Miscellaneous	149,935	3,886
Total	198,539,322	1,733,176

These mines were located in 14 states with production being distributed as shown in Table 15. The 25 leading primary gold-producing mines in the United States which account for more than 97 percent of the gold production are listed in Table 16.

A breakdown of the data shown in the prior tabulation indicates the relative importance of the various sources of gold to the industry.

	Troy Ounces Recovered	Percent of Total
Placer Mines	25,418	1.4
Gold Mines	1,031,050	59.5
Gold-Silver Mines	1,883	0.1
Silver Mines	2,900	0.2
Copper Mines	579,171	33.4
Lead Mines	3,069	0.2
Zinc Mines	1,057	0.1
Copper-Lead-Zinc Mines	84,742	4.9
Miscellaneous	3,886	0.2
Total	1,733,176	100.0

The gold industry is a relatively minor direct contributor to the

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TABLE 15. PRODUCTION OF GOLD IN THE UNITED STATES IN 1969, BY STATES, TYPES OF MINES, AND CLASSES OF ORE YIELDING GOLD, IN TERMS OF RECOVERABLE METAL (19)

State	Placer (troy ounces of gold)	Lode: Gold ore — Short tons	Lode: Gold ore — Troy ounces of gold	Lode: Gold-silver ore — Short tons	Lode: Gold-silver ore — Troy ounces of gold	Lode: Silver ore — Short tons	Lode: Silver ore — Troy ounces of gold
Alaska	21,146	(1)	75	------	------	------	------
Arizona	5	512	500	63,565	139	75,487	153
California	2,650	[2] 6,263	[2] 4,739	(3)	(3)	126	3
Colorado	1,056	100	70	515	86	3,583	63
Idaho	3	[4] 58	[4] 75	(3)	(3)	531,313	887
Montana	4	[5] 7,086	[5] 7,479	(3)	(3)	36,242	986
Nevada	2	1,380,771	378,934	------	------	5,081	264
New Mexico	1	------	------	1,287	502	------	------
Oregon	W	[6] 854	[6] 875	(3)	(3)	------	------
South Dakota	W	1,934,622	[6] 593,146	------	------	------	------
Utah	------	------	------	142,738	1,156	2,842	544
Other States	------	62,237	45,708	------	------	------	------
Total	25,418	3,392,503	[7] 1,031,050	208,105	1,883	654,674	2,900
Percent of total gold	1	------	59	------	(1)	------	(1)

State	Lode: Copper ore — Short tons	Lode: Copper ore — Troy ounces of gold	Lode: Lead ore — Short tons	Lode: Lead ore — Troy ounces of gold	Lode: Zinc ore — Short tons	Lode: Zinc ore — Troy ounces of gold
Alaska	------	------	50	6	------	------
Arizona	107,774,696	108,718	218	106	------	------
California	------	------	[6] 104,338	[6] 391	------	------
Colorado	------	------	982	97	277,350	873
Idaho	542	5	[7] 255,785	[7] 1,555	(3)	(3)
Montana	16,016,901	15,420	[7] 2,879	[7] 267	(3)	(3)
Nevada	14,345,225	76,212	4,519	615	------	------
New Mexico	12,491,450	8,163	------	------	221,563	182
Oregon	------	------	------	------	------	------
Utah	38,650,300	370,632	534	32	------	------
Other States	389	21	------	------	261,144	2
Total	189,279,503	579,171	369,355	3,069	760,057	1,057
Percent of total gold	------	33	------	(1)	------	(1)

State	Lode: Copper-lead, lead-zinc copper-zinc, and copper-lead-zinc ores — Short tons	Lode: Copper-lead, lead-zinc copper-zinc, and copper-lead-zinc ores — Troy ounces of gold	Lode: Old tailings, etc. — Short tons	Lode: Old tailings, etc. — Troy ounces of gold	Lode: Total — Short tons	Lode: Total — Troy ounces of gold	Refinery production [12] (troy ounces of gold)
Alaska	------	------	------	------	50	21,227	18,900
Arizona	106,783	30	91,744	[8] 1,227	108,113,005	110,878	114,900
California	(3)	(3)	417	[8] 121	111,194	7,904	7,250
Colorado	741,484	[9] 23,532	------	------	1,024,014	25,777	26,200
Idaho	677,039	875	600	3	1,465,337	3,403	3,400
Montana	1,068	9	5,435	24	16,069,611	24,189	20,000
Nevada	2,749	28	14,844	239	15,753,189	456,294	452,500
New Mexico	54,413	102	76	2	12,768,789	8,952	10,000
Oregon	------	------	------	------	854	875	350
South Dakota	------	------	------	------	1,934,622	593,146	593,200
Tennessee	1,574,140	126	------	------	1,574,140	126	110
Utah	567,514	60,040	36,786	981	39,400,714	433,385	425,000
Other States	------	------	33	[10] 1,289	323,803	47,020	[13] 45,010
Total	3,725,190	84,742	149,935	3,886	198,539,322	1,733,176	1,716,850
Percent of total gold	------	5	------	(1)	------	100	------

W Withheld to avoid disclosing individual company confidential data; included in placer total and in lode ores as noted.

[1] Less than ½ unit.
[2] Gold and gold-silver ores combined to avoid disclosing individual company confidential data.
[3] Placer combined with gold and gold-silver ores to avoid disclosing individual company confidential data.
[4] Placer combined with gold ore to avoid disclosing individual company confidential data.
[5] Excludes Oregon and South Dakota placer production; included in placer total.
[6] Lead and lead-zinc ores combined to avoid disclosing individual company confidential data.
[7] Lead and zinc ores combined to avoid disclosing individual company confidential data.
[8] Includes byproduct gold recovered from uranium ore.
[9] Includes byproduct gold recovered from tungsten ore.
[10] Includes byproduct gold recovered from fluorspar ore.
[11] Includes byproduct gold recovered from magnetite-pyrite ore.
[12] Source: U.S. Bureau of the Mint.
[13] Washington only.

TABLE 16. TWENTY-FIVE LEADING GOLD-PRODUCING MINES IN THE UNITED STATES IN 1969, IN ORDER OF OUTPUT (19)

Rank	Mine	County and State	Operator	Source of gold
1	Homestake	Lawrence, S. Dak	Homestake Mining Co	Gold ore.
2	Utah Copper	Salt Lake, Utah	Kennecott Copper Corp	Copper, gold-silver ores.
3	Carlin	Eureka, Nev	Carlin Gold Mining Co	Gold ore.
4	Cortez	Lander, Nev	Cortez Gold Mines	Do.
5	Veteran-Tripp	White Pine, Nev	Kennecott Copper Corp	Copper ore.
6	Mayflower	Wasatch, Utah	Hecla Mining Co	Copper-lead-zinc ore.
7	Knob Hill	Ferry, Wash	Knob Hill Mines, Inc	Gold ore.
8	Copper Queen-Lavender Pit	Cochise, Ariz	Phelps Dodge Corp	Copper ore.
9	New Cornelia	Pima, Ariz	do	Copper, gold-silver ores.
10	San Manuel	Pinal, Ariz	Magma Copper Co	Copper ore.
11	Idarado	Ouray and San Miguel, Colo	Idarado Mining Co	Copper-lead-zinc ore.
12	Copper Canyon	Lander, Nev	Duval Corp	Copper ore.
13	Berkeley Pit	Silver Bow, Mont	The Anaconda Company	Do.
14	Morenci	Greenlee, Ariz	Phelps Dodge Corp	Copper, gold-silver ores.
15	Hogatza River	Yukon River Region, Alaska	United States Smelting Refining and Mining Co	Placer.
16	Magma	Pinal, Ariz	Magma Copper Co	Copper ore.
17	U.S. and Lark	Salt Lake, Utah	United States Smelting Refining and Mining Co	Lead, lead-zinc ores.
18	Sunnyside	San Juan, Colo	Standard Metals Corp	Lead-zinc ore.
19	Eureka	Madison, Mont	Pacific Mines, Inc	Gold-silver ore.
20	Oriental	Sierra, Calif	Dickey Exploration Co	Gold ore.
21	Continental	Grant, N. Mex	United States Smelting Refining and Mining Co	Copper ore.
22	Christmas	Gila, Ariz	Inspiration Consolidated Copper Co	Do.
23	Pacific	Madison, Mont	Pacific Mines, Inc	Gold-silver ore.
24	Chino	Grant, N. Mex	Kennecott Copper Corp	Copper ore.
25	Ray Pit	Pinal, Ariz	do	Do.

economy. It has been estimated that gold-mining operations per se employ about 3000 to 3500 people, and, in addition, about 700 to 800 people are employed in the base-metal industries to recover and refine the by-product gold from copper, lead, etc., ores.

Raw Materials and Processes

Ores

Gold is widely distributed in nature in both native and combined form. The principal ore mineral is "native" or metallic gold, which occurs in association with quartz and other rocks. Native gold, almost invariably containing minor quantities of silver, may occur as perceptible grains, flakes, sheet, or wire in veins of quartz and other minerals or in a finely divided state disseminated in the ores of copper, lead, and occasionally zinc.

When rocks or deposits containing gold are dissolved and disintegrated by "weathering" (i.e., rain, freezing, erosion, etc.), the gold particles resistant to these forces are liberated and washed into waterways. Owing to the high specific gravity of the gold, it tends to settle and becomes concentrated by hydraulic action in stream beds, in layers. Often, over the ages, such forces have produced concentrations of "free gold" that can be profitably recovered. This is the so-called "placer" gold ore and is distinguished from "lode" ore in which the gold is still associated, encapsulated, etc., in other rocks.

Mining

Gold-mining methods vary widely, depending on the size, shape, and depth of a deposit, the associated minerals, economic considerations, etc.

Two broad types of mining must be distinguished. These are "placer" mining and "lode" mining.

Placer mining, which accounts for a relatively small but still significant amount of gold production, is applied to "placer" deposits. These may be described as unconsolidated deposits of detrital material resulting from the weathering of rock containing gold in economically important concentration, together with sand, gravel, and other minerals, resulting from the degradation of the original rock. They may exist in currently running water or they may be the dried out relics of a stream that changed its course or ceased to exist ages ago.

Gold placer deposits were mined originally in this country by the 49'ers,

in California, employing small-scale hand methods, such as pans, sluice boxes, rockers, etc. Some small-scale placer mining by individuals is still practiced. Large-scale placer mining, employing draglines, bucket dredges, hydraulic dredges, etc., accounts for most of the gold recovery by this mining method.

The objectives of both large and small-scale placering is the same--to eliminate the worthless waste rock and to collect gold in a high-grade concentrate. The principle employed is the same in both cases. The ore is removed from the deposit by the most convenient and economic means available. This includes excavation with shovels or draglines, by hydraulic methods (i.e., by breaking up the poorly consolidated material with high-pressure streams), by bucket dredging, or by suction dredging. The ore is then transported to a washing plant by bucket elevators, through sluices, prepared channels, or through lines to a screening and washing plant.

Washing plants may be placed on land or may be afloat, often on the dredges themselves. The objectives of screening and washing are to clean and remove from the circuit the larger rocks and boulders. The screening and washing is commonly done in trommels, which are rotating horizontal cylinders, with perforations of a size and frequency selected to permit the immediate rejection of barren rock oversize. The smaller rocks, sand, heavy minerals, and gold pass through these apertures and are treated by methods which take advantage of the high specific gravity of gold. These include sluice boxes, tables, jigs, etc. In some cases mercury may be employed to increase gold recovery by amalgamating with fine gold particles which might escape the concentrating operation.

Placer mining produces a still impure gold concentrate which may first be treated by amalgamation, melting, fluxing, etc., to produce high-purity gold bars, or which may be sent to gold refineries.

Placer gold in arid locations is, in some cases, concentrated by dry methods, using air instead of water to wash away lighter materials. These are small operations.

The mining of lode ores of gold is done through shafts and adits by many of the conventional methods of underground mining. The major U.S. gold mine, which produces about 60 percent of the country's gold, employs cut and fill stoping methods in which mined out stopes are filled with mill tailings. In recent times, open-pit mining of gold ore has been practiced in Nevada. As mentioned previously, about one-third of the gold produced in the United States is as a by-product from copper, lead, and zinc mines. Mining practices have been discussed elsewhere.

Recovery

The recovery of gold from lode gold mines is done by any one or

combination of several methods selected and designed to yield maximum economic recovery.

Unlike placer gold, however, lode gold has not been preconcentrated by the forces of nature and has not been liberated from its host rock. Accordingly, all lode gold mines preface recovery processes by crushing and grinding to liberate gold physically or make it accessible to chemical solutions.

After crushing and grinding, roasting may be necessary. Treatment may be by any one or a combination of three methods. These are:

1. Gravity methods such as riffling or jigging as is applied to placer gold deposits. It is believed that very few of the lode gold operations now employ this procedure.

2. Amalgamation. Gold with clean surfaces dissolves rapidly in mercury to form an amalgam. Amalgamation is generally carried out by feeding mercury into the grinding circuit to form an amalgam with the gold as it is liberated. The slurry of crushed ore in water is then passed over large copper plates previously coated with mercury. Amalgam from the ore collects and builds up on these plates. They are then periodically scraped by hand with rubber scrapers to remove the accumulated gold-mercury amalgam. This amalgam is then placed in retorts and the mercury vaporized and condensed and recovered for reuse. The residue from retorting is crude gold and is sent to a furnace refining operation.

3. Cyanidation. Gold ore, as mined, or the residue containing gold which escaped amalgamation from the amalgamation process is subjected to a leaching process in which dilute aqueous sodium cyanide solution (about 0.02 to 0.05 percent) is the solvent. This form of leaching, called cyanidation, is done in tanks. Agitation and the necessary oxygen is supplied by bubbling air through the slurry. The reaction occurring during leaching is

$$4Au + 8NaCN + 2H_2O \rightarrow 4Na\ Au(CN)_2 + 4NaOH.$$

The cyanide leach liquor is filtered from the residue and the filtrate is treated with zinc dust to precipitate the gold as metallic particles according to the reaction:

$$NaAuCN_2 + 2NaCN + Zn + 2H_2O \rightarrow NaZnCN_4 + Au + H_2 + 2NaOH.$$

The gold particles are recovered by filtering and the clear solution returned to the leaching operation.

Refining

The impure gold recovered from either the amalgamation or cyanidation

is refined by treatment in the so-called Doré furnace. In this operation the material is melted with appropriate fluxes (soda ash, borax, silica, etc.) under oxidizing conditions to produce a gold-base alloy which may still contain silver and the platinum group metals and a slag which will contain impurities such as copper, zinc, etc.

If platinum-group metals are absent or virtually so, the Doré metal is purified while still molten by the Miller process, in which chlorine is bubbled through the charge. This treatment volatilizes base metals which may be present and converts silver to molten silver chloride salt which rises to the top of the melt and can be poured or skimmed from the gold. Refined gold made by this process generally contains about 99.6 percent gold, and is suitable for many purposes.

If platinum metals are present or if higher purity is desired, the Doré metal is cast into small anodes and electrolyzed in chloride solution by a miniaturized method analogous to the refining of copper by electrolysis. In this, the Wöhlwill process, gold is electrolytically oxidized as the anode passes into solution and is deposited in pure form on the cathode. The resulting cathode is melted and cast into bars of 99.9+ percent purity. In the Wöhlwill process, silver is also electrolytically oxidized at the anode, but is quickly and almost completely converted to insoluble silver chloride.

Gold by-products obtained from the processing of lead, zinc, and copper ores are generally given special pretreatments to eliminate base-metal impurities. Eventually in these processes a Doré alloy is formed which is then treated by refining techniques for gold as described above, or, if significant silver is present, by the processes of electrolysis described in the section of this report on silver.

Size and Characteristics of the Silver Industry

About two-thirds of domestic silver produced in 1969 was a by-product of copper, lead, and zinc ores. Most of the remainder came from mines worked principally for their silver values. Gold-silver ores, accounted for about 1 to 2 percent of silver production.(20)

Twenty-five leading silver producers contributed 80 percent of the total domestic output. These are listed in Table 17. Production data by states for 1969 are shown in Table 18.

It has been estimated by the Bureau of Mines that the mining and milling segment of the silver industry employs less than 2000 people. No estimate has been advanced for employment in the metal-recovery and refining segment of the industry owing to its complex interrelationship with base-metal smelting and refining practice.

Forecasts indicate that primary silver demand in the United States in

TABLE 17. TWENTY-FIVE LEADING SILVER-PRODUCING MINES IN THE UNITED STATES IN 1969, IN ORDER OF OUTPUT[20]

Rank	Mine	County and State	Operator	Source of silver
1	Sunshine	Shoshone, Idaho	Sunshine Mining Co	Silver ore.
2	Utah Copper	Salt Lake, Utah	Kennecott Copper Corp	Copper, gold-silver ores.
3	Galena	Shoshone, Idaho	American Smelting and Refining Co	Silver ore.
4	Lucky Friday	....do	Hecla Mining Co	Lead ore.
5	Berkeley Pit	Silver Bow, Mont	The Anaconda Company	Copper ore.
6	Bunker Hill	Shoshone, Idaho	The Bunker Hill Co	Lead-zinc ore, silver tailings.
7	Crescent	....do	....do	Silver ore.
8	White Pine	Ontonagon, Mich	White Pine Copper Co	Copper ore.
9	Bulldog	Mineral, Colo	Homestake Mining Co	Silver ore.
10	U. S. and Lead	Salt Lake, Utah	United States Smelting Refining and Mining Co	Lead, lead-zinc ores.
11	Copper Queen-Lavender Pit	Cochise, Ariz	Phelps Dodge Corp	Copper ore.
12	Idarado	Ouray and San Miguel, Colo	Idarado Mining Co	Copper-lead-zinc ore.
13	Pima	Pima, Ariz	Pima Mining Co	Copper ore.
14	Mayflower	Wasatch, Utah	Hecla Mining Co	Copper-lead-zinc ore.
15	Mission	Pima, Ariz	American Smelting and Refining Co	Copper ore.
16	Butte Hill Copper Mines	Silver Bow, Mont	The Anaconda Company	Do.
17	Morenci	Greenlee, Ariz	Phelps Dodge Corp	Copper, gold-silver ores.
18	Mineral Park	Mohave, Ariz	Duval Corp	Copper ore.
19	Copper Canyon	Lander, Nev	....do	Do.
20	Magma	Pinal, Ariz	Magma Copper Co	Do.
21	Burgin	Utah, Utah	Kennecott Copper Corp	Lead, lead-zinc ores.
22	New Cornelia	Pima, Ariz	Phelps Dodge Corp	Copper, gold-silver ores.
23	United Park City	Summit and Wasatch, Utah	United Park City Mines Co	Lead-zinc ore.
24	Darwin	Inyo, Calif	West Hill Exploration, Co	Do.
25	Dayrock	Shoshone, Idaho	Day Mines, Inc	Lead ore.

TABLE 18. MINE PRODUCTION OF RECOVERABLE SILVER BY STATES IN 1969[20]

States	Troy Ounces
Alaska	2,030
Arizona	6,141,022
California	491,927
Colorado	2,598, 63
Idaho	18,929,697
Maine	319,718[a]
Michigan	1,009,022
Missouri	1,442,090
Montana	3,429,314
Nevada	884,155
New Mexico	465,591
New York	31,755
Oklahoma	Combined with Maine
Oregon	4,749
Pennsylvania	Combined with Maine
South Dakota	124,497
Tennessee	78,614
Utah	5,953,567
Wyoming	Combined with Maine
Washington	Combined with Maine
Total	41,906,311

(a) Production of Maine, Oklahoma, Pennsylvania, Washington, and Wyoming (1969) combined to avoid disclosing individual company confidential data.

the year 2000 will range from 280 to 560 million troy ounces with a median of 420 million troy ounces. Present demand (1969) is about 160 million troy ounces.

Raw Materials and Processes

Minerals of silver are shown in the following tabulation:

Argentite	Ag_2S
Polybasite	Ag_9SbS_3
Proustite	Ag_3AsS_3
Slephanite	Ag_5S_4Sb
Pynargyrite	Ag_3SbS_3
Cerargynite	AgCl
Native silver	Ag
Silver-bearing tetrahedrite	$(Cu\text{-}Ag)Sb_2S_7$.

The major ore mineral in the United States is silver-bearing tetrahedrite associated with sulfides of copper, lead, and zinc. Silver-bearing ores vary in silver content from the extremely low levels found in major copper deposits to grades in which silver is the main component.

As mentioned previously, much of the primary silver produced in the United States is as a by-product of copper, lead, and zinc mining. The mining of ores in which the principal value is silver is generally done by underground methods.

Recovery of Silver From Copper Ores

Figure 10 outlines routes for the recovery of silver and gold. Silver and gold follow copper through all stages of concentration, smelting, and fire refining (1). When copper is refined electrically, however, these metals, together with selenium, tellurium, etc., collect as finely divided solids in the electrolytic tank. These are called slimes (2) (see section on copper). Slimes, as produced, contain high percentages of fine copper and are first leached in hot dilute sulfuric acid (3), to dissolve excess copper, and some tellurium and selenium, away from the silver and gold (4). Typically, such leached slimes will contain about 10,000 ounces of silver per ton, with varying proportions of gold, lead, selenium, arsenic, antimony, etc., depending on the characteristics of the original ore (5). The treated slimes are then smelted in a small reverberatory furnace, called a Doré furnace (6) with various fluxes such as limestone, borax, fluorite, silica, etc., selected to produce a fluid slag of the base metals so that they may be separated from the bulk of the molten silver and gold. This slag (7) normally contains significant amounts of gold and silver and to recover these values it is usually returned to the copper smelter. The gold and silver alloy,

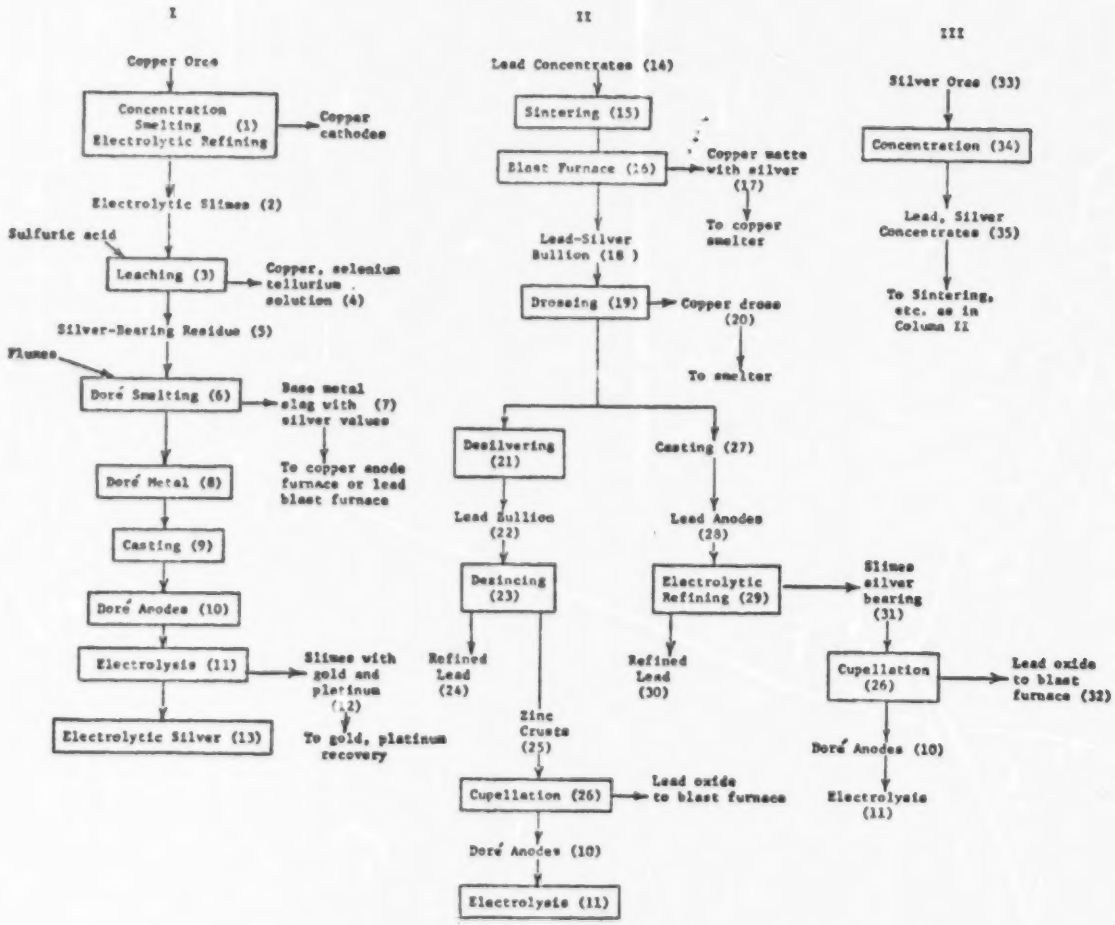

FIGURE 10. PROCESSES FOR RECOVERING SILVER

now rid of most of its base metal and metalloid impurities, is called Doré metal (8). Typically such an alloy will contain 90 or more percent of silver, gold, platinum, and a small amount of copper. The molten Doré metal is cast into small anodes (10). These are electrolyzed in small specialized cells in nitrate solution (11). Two main types of electrolytic cells are used. In one type, the Thum cell, carbon cathodes constitute the floor of the cell, and the impure silver anodes are suspended in a shallow receptacle with a cloth bottom. On electrolysis in this type of cell, the silver dissolves anodically and is deposited in small crystals on the bottom cathode. These crystals are raked either manually or mechanically from the cell, washed, and dried (13). During the electrolysis, gold and platinum do not dissolve but collect as slimes on the cloth bottom of the anode receptacle (12). These are sent to further processing for the recovery of these metals.

The electrolytically refined silver crystals (13)--which will exceed 99.9 percent purity--subsequently are melted and cast into bars weighing about 100 pounds. Another type cell called the Moebius cell is also used in silver refining. In this cell the anodes are enclosed in cloth bags and suspended alternately between cathodes. During electrolysis in the nitrate solution, the silver is anodically dissolved and deposits as loosely adherent crystals on the cathodes. These are periodically scraped off mechanically into a basket on the bottom of the cell. The gold and platinum slimes in the Moebius cell are retained in the anode bags.

Recovery of Silver From Lead Concentrates

The recovery of silver from ores in which lead and zinc are the major components by weight is less straightforward than the recovery from copper ores. Silver follows copper through to the electrolytic refining step in copper metallurgy. In lead metallurgy, however, silver may follow several routes. After lead concentrates are sintered (15) and smelted in the blast furnace (16), a portion of the silver will accompany the copper matte that is normally formed. This matte (17) is returned to copper smelters for the recovery of both silver and copper as outlined in Column I of Figure 10. Much of the silver, however, accompanies lead in a bullion (18). Bullion from most ores contains enough gold and silver to make their extraction profitable. In addition, it contains undesirable impurities such as copper, zinc, tin, antimony, and arsenic which must be removed by refining. The processing steps for refining lead will vary with the composition of the impure bullion and the end product desired. The steps shown in Column II from the drossing step on are typical.

Drossing (19) consists in holding the molten bullion at a temperature just above the melting point, during which operation copper rises to the top and is skimmed off. The last traces of copper are removed by adding sulfur. The copper dross is returned to a copper smelter for

copper recovery and the recovery of whatever silver may have accompanied the copper dross. Arsenic, antimony, and tin are subsequently oxidized and are volatilized or skimmed from the surface of the lead.

After drossing, two routes are available for the production of refined lead. One, essentially fire refining, includes a silver and gold recovery procedure involving the addition of zinc metal to the molten lead (21, 22, 23, 25, 26). When zinc is added in the desilvering step, the precious metals alloy with the zinc and rise to the surface. The last traces of zinc in the lead are removed either by vacuum distillation or by fluxing with caustic soda (23). The zinc fraction or zinc crusts (25) removed from the lead are dezinced by distillation or vacuum, then "cupelled" (26) in a small reverberatory furnace under strongly oxidizing conditions to convert the lead to molten lead oxide which carries off other materials besides some silver and gold. Lead oxide with its burden of impurities such as zinc, arsenic, antimony, etc., is returned to the lead blast furnace. The molten gold and silver remains in the cupel furnace as Doré metal, and is cast into anodes for treatment as shown in Column I of Figure 10 (10-11).

Another path for producing refined lead after the drossing operation is by electrolytic refining (29). This technique has been described in the section of Volume I of this report dealing with lead. Electrolytic refining generally is employed when undesirably high concentrations of bismuth are present. During the electrolysis of lead, silver and gold, as in copper electrolysis, separate as slimes. These are collected and subjected to cupellation (26) and electrolysis (27) as described previously.

Recovery of Silver From "Silver Ores"

As explained previously, some ores have predominant silver values, but in all cases, the quantity of silver involved is much less than that of base metals, such as lead. Such ores are first concentrated by flotation processes (34) as described elsewhere in this report. Concentrates then are treated by the processes outlined in Columns I and II (Figure 10) to recover silver.

Waste Water in the Gold and Silver Industries

Responses to this survey were provided by only two gold mines. One mine took in 66 million gallons per year and discharged no water. This type of situation is analogous to the numerous examples of "tailings-pond"-type operations in desert climates, whose characteristics are discussed in greater detail in Volume I of this report dealing with copper, lead, and zinc. Briefly, however, the water-usage pattern involves the use of major portions of the water in the ore-concentrating process,

with all water from all other uses (boiler, sanitary, dust control, etc.) being discharged to the common receiver of the tailings pond from which water is recycled to the ore-processing operation. In desert climates, evaporation from the large surface area of the pond and seepage into the ground result in zero discharge.

The other gold-producing operation contributing to this program ran a uniquely identifiable operation and so cannot be treated within the constraints of this report.

A recent journal article described the current situation of the Homestake mine with regard to water-pollution problems.[21] The mine and concentrator were designed to use the dual amalgamation-cyanidation process on an ore with gold content of 0.3 ounce per ton, achieving a reported 95 percent efficient recovery rate, with 62 percent recovered by mercury amalgamation and 33 percent by cyanide leaching.

The tailings slurry, using the dual process, was reportedly discharged untreated at a rate of 1700 gpm, and containing 5,600 tons of solids per day and 10 to 40 pounds of mercury. At the end of 1970, the plant suspended the use of the amalgamation process and used only cyanidation, with a reported loss of 75 pounds (3 percent) of the 2500-pound daily use, about 50 pounds as cyanide and 25 pounds ad cyanate. The analyses of waste waters reported mercury and cyanide as follows:

	Location	Mercury, ppb	Free Cyanide, ppm
Jan., 1971 Leach Process	Whitewood Creek below discharge	--	2.6
	@ 25 to 30 miles below discharge	--	0.05
Dual Process	Whitewood Creek at Deadwood	96.0	
	Whitewood Creek 25 to 30 miles below	67.0	
	Belle Fourche River	12.0	
	At Bridger on Cheyenne River (estimated 100 to 150 miles downstream)	1.1-1.8	

The current leach practice is achieving a recovery of less than 94 percent.

A considerable portion of the article was devoted to the varying assessments of the effects of the discharges. It would appear that, through process modification, the mercury content of the effluent has been reduced to zero. The development of a treatment process to control the ported discharge of free cyanide is under way. The estimated pollution-control cost of $3 million is about 15 percent of the nominal value of annual production, i.e., $20,265,000.

SECTION VIII

THE PRIMARY MOLYBDENUM AND TUNGSTEN INDUSTRIES

Size and Characteristics of the Molybdenum Industry

The raw ore concentrates from which molybdenum is extracted may be considered to arise from two sources: those mining and concentrating operations producing molybdenum as the principal product and those operations producing molybdenum as a by-product. The former category consists of two operations, while by-product molybdenum concentrates are produced chiefly in association with copper production from porphyry ore deposits and to lesser extents with uranium and tungsten operations. The principal producers of molybdenum concentrates are listed in Table 19. The first two entries in the table are operations where molybdenum is the principal product; the balance of the operations produce molybdenum as a by-product of copper. Total production in 1969 amounted to 100 million pounds or 50,000 tons of contained molybdenum. The molybdenum in these concentrates is converted to various compounds, alloys, and the pure metal. The amounts, forms, and end uses listed by the Bureau of Mines for 1969 are listed in Table 20. This breakdown of consumption shows that the greatest usage of molybdenum is in the oxide form and in the form of ferromolybdenum, both for use in the steelmaking industry. A relatively small portion of the total molybdenum production is reduced to the form of pure molybdenum metal or molybdenum-base alloys. In any event, metallic molybdenum is produced from the oxide form, one step removed from the naturally occurring sulfide form.

Raw Materials and Processes[23]

The two most important mineral forms of molybdenum are molybdenite, MoS_2, or wulfenite, $PbMoO_4$. An example of a commercially important deposit of molybdenite is the Climax Mine in Colorado where the ore contains 0.6 percent molybdenite. The other major operation in the United States is that at Questa, New Mexico, where the important mineral is wulfenite. Molybdenite (sulfide) is the form associated with the concentrating-grade copper sulfide ores and is the form of the by-product concentrate produced by differential flotation at many copper-producing operations.

Molybdenum disulfide mineral concentrates produced as by-products from porphyry copper operations constitute the sole source at present of the metal rhenium. Rhenium is recovered from the flue dust during the roasting of the molybdenum sulfide to the oxide form. Rhenium is not recovered from the minerals of the principal molybdenum mines, i.e.,

TABLE 19. - PRINCIPAL PRODUCERS OF MOLYBDENUM CONCENTRATES IN THE UNITED STATES(22)

Company	Location	Production (Contained Molybdenum), millions lb/yr
American Metal Climax, Inc.	Climax Colo. Empire, Colo.	60
Molybdenum Corporation of America	Questa, N. Mexico	10.9
Duval Sierrita Corp.	(Sauhorita, Ariz.) Mineral Park, Ariz.	5.7(a)
Kennecott Copper Corp.	Various	15.9
American Smelting and Refining Co.	Arizona	1.2
Pima Mining Co.	Arizona	1.7
Bagdad Copper Corp.	Bagdad, Arizona	0.408

(a) When the Sierrita operation reaches full capacity, an annual production rate of 13 million pounds of molybdenum is expected.

TABLE 20. AMOUNTS, FORMS, AND END USES OF MOLYBDENUM CONSUMED (1969) [22]

(Thousands of Pounds of Contained Molybdenum)

End Use	Oxides	Ferro-molybdenum	Molybdates	Other Forms	Total[a]
Steels and cast irons	29,190	9,004	--	466[a]	38,660
Superalloys	338	597	--	1,581	2,516
Specialty alloys	--[a]	470[a]	--	141[a]	611[a]
Metal powder products	412	--[a]	--	1,899	1,311
Chemicals, pigments, ceramics, catalysts and others	2,280	--[a]	371	785	3,436
Miscellaneous	2,128	1,065	418	478	4,089
Totals[a]	34,349	11,135	789	5,348	51,622

(a) Totals and entries arranged to avoid disclosure of individual company data. Totals include data withheld.

its recovery has been limited to copper ores.

The general route followed from mineral to product consists of the conversion of the sulfide to a crude (but salable) oxide, by roasting, the purification of the oxide by sublimation to produce yet another product form, and for a small portion of total production, the conversion of the pure oxide to metal or to ammonium molybdate, which may then be converted to metal.

The production of molybdenum from ore deposit to oxide or metal product follows the general sequence of mining, crushing, grinding, flotation concentration, and furnacing of concentrates to produce oxide and eventually the metal.

Mining and Concentrating

Molybdenum ores are mined by both open pit and underground methods. Generally standard mining methods, discussed in more detail in the portion of this report dealing with copper, lead, and zinc, are used in molybdenum operations. The most recent entries into the molybdenum-producing field may serve as examples of methods.

The Sierrita Property of the Duval Corporation in Arizona is a large open-pit mining operation mining an ore containing 0.35 percent copper and 0.036 percent molybdenum. Ore-mining and -concentrating capacities are to process 85,000 tons of throughput per day. The ore is blasted loose, loaded with power shovels, trucked to a primary crusher which discharges to a conveyer belt, and conveyed 2-1/2 miles to the mill. The ore is then processed through secondary and tertiary crushers and wet ground in ball mills. The ground ore is floated to produce a rougher concentrate which is reground and floated again to produce a concentrate containing both copper and molybdenum minerals. This concentrate is then conditioned and subjected to another flotation operation in which the molybdenum mineral is floated and the copper mineral depressed. Both concentrates are dewatered by thickeners and filters and shipped. The molybdenum sulfide concentrate is either sold as is for use as the sulfide or sold for roasting to the oxide.

Processing of Concentrates

The various product forms of molybdenum and the processes used to produce them are indicated in Figure 11.

The conversion of molybdenum sulfide concentrates to crude molybdenum oxide is achieved in a manner similar to that for almost all other sulfide ores--by roasting in circular hearth furnaces. In the case of molybdenum roasting, the desired reaction is the complete oxidation of

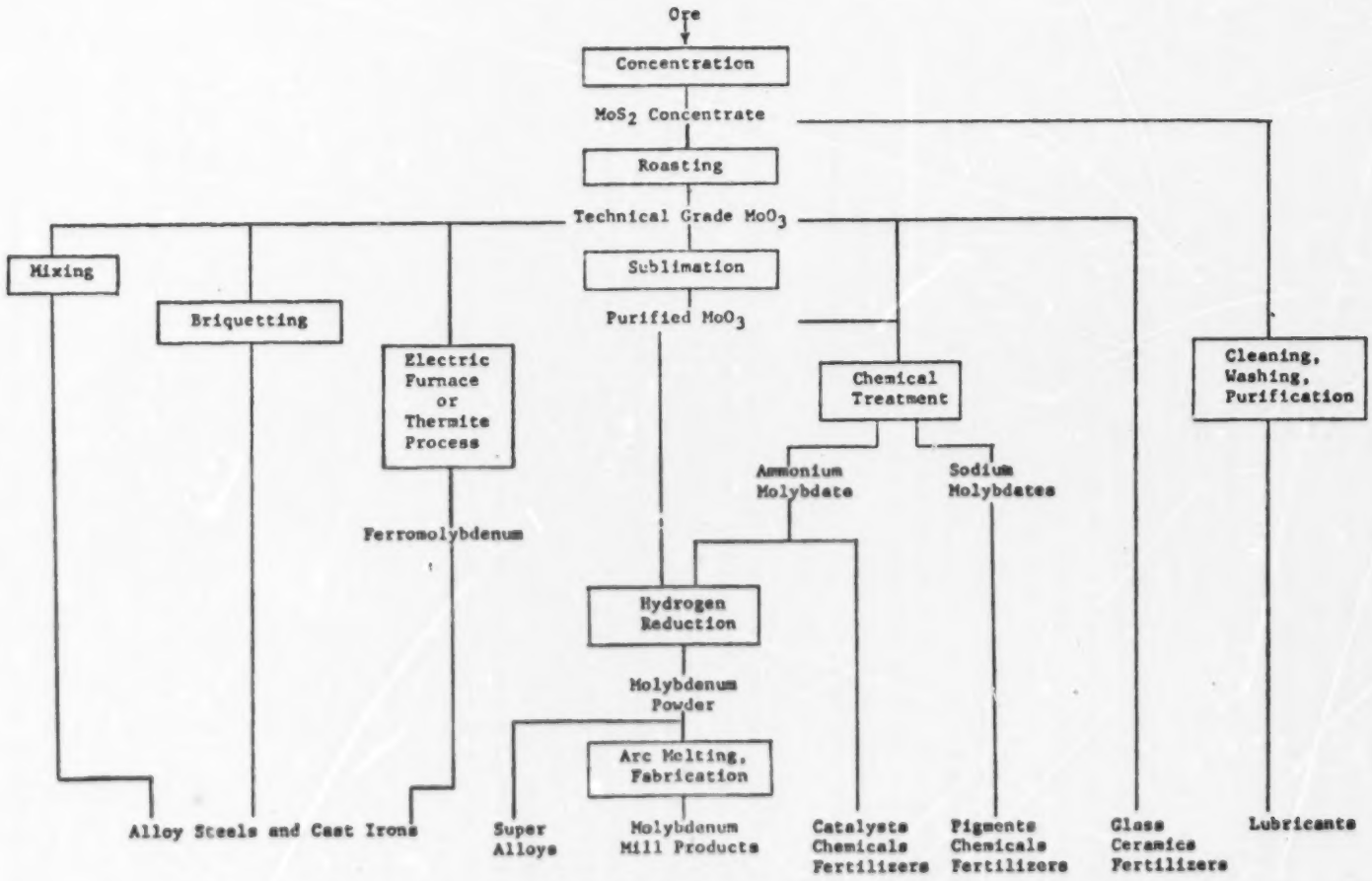

FIGURE 11. DIAGRAM OF PROCESSES AND PRODUCTS IN THE MOLYBDENUM INDUSTRY[23,24]

all sulfur and production of the higher oxide, MoO_3. The oxidation reaction is self-sustaining, but the significant volatility of the oxide at about 1300 F requires that the temperature be controlled by limit losses. An example of a molybdenum sulfide roasting operation would thus include a Nichols-Herreschoff 12-hearth circular roasting furnace. The molybdenum sulfide concentrate is introduced to the upper hearth, and mixed by rotating rakes to successive lower hearths. The furnace is operated at a slight vacuum (< 0.1 inch of water) so that air is drawn in at the lower hearth and is withdrawn from several of the middle hearths where the major heat of reaction is generated. The off-gas contains the products of combustion and SO_2. The upper hearths operate at 800 to 900 F as the concentrate is preheated and volatiles are driven off, the center hearths operate at 900 to 1100 F where the major reaction occurs, and the lower hearths are maintained at 500 to 900 F by supplementary gas heating to ensure that sulfur is reduced to about 0.05 to 0.25 percent. The product, withdrawn from the bottom hearth of the roaster, is known as technical-grade molybdic oxide. This form of oxide usually contains most of the impurities present in the original concentrate and is thus defined only by a specification requiring a minimum of 60 percent molybdenum, with maximum impurity levels specified for copper (0.50 percent), lead (0.15 percent), phosphorus (0.05 percent), and sulfur (0.25 percent).

Purified molybdic oxide, containing on the order of 99.5 to 99.975 percent MoO_3, is produced by heating of technical-grade oxide in a furnace to temperatures of 1800 to 2150 F, which results in the sublimation or vaporization of the oxide. The vapors are carried in a stream of forced air from the furnace, through ducts and cooling flues to a fabric filter collector, e.g., a wool fabric baghouse. The sublimation is usually accomplished in a muffle-type furnace with a controlled, forced-air draft system, and in the case of one large producer, a circular furnace with a rotating hearth, so that crude oxide and residue may be continuously charged and withdrawn, respectively. The sublimation process used to produce purified molybdic oxide may be iterated to increase purity to high levels.

An alternative method of achieving high-purity forms of molybdenum is to dissolve purified (once-sublimed) molybdic oxide in ammonium hydroxide solution. The solution is filtered and evaporated to crystallize pure ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. This process is characterized as producing the purest form of commercially available molybdenum.

Either the trioxide or ammonium molybdate may be reduced to elemental metal by heating to a temperature of 1800 to 2000 F in a hydrogen atmosphere. The specific choice of starting materials and reduction conditions (e.g., single or two-stage reduction) depends on such conditions as initial purity of the starting materials.

The hydrogen reduction of oxide particles or ammonium molybdate crystals is the most common method used to produce molybdenum metal. The product of reduction is metal powder. The processing of the powder to ordinary

metal forms of sheet, bar, etc., can be accomplished by two routes. One, the powder metallurgy route, involves the compaction of the powders into appropriate sized blocks, cylinders, or other preforms, followed by high-temperature heat treatment to accomplish the sintering or bonding of the particles. Subsequent steps of processing apply heat and pressure either separately as in the compacting and sintering stages, or simultaneously as in a hot forging or other hot-working process to consolidate the powder, eliminate any porosity, and eventually produce a completely solid, wrought product form.

The alternative route involves the initial hot or cold compaction and sintering of the powder into long bars, which serve as consumable electrodes in an arc-melting process. In an appropriate furnace, consisting chiefly of a water-cooled copper crucible, the preformed bars serve as one electrode for striking a high-current, low-voltage arc between the bar, and a starting pad of molybdenum metal. As the bar is progressively melted by the arc, the molten metal falls through the arc and forms an ingot, which progressively freezes into solid form. The ingot may be remelted to improve purity or quality and then fabricated to product form.

Calcium molybdate no longer is made in the strict sense of chemical terminology. The current form of product to which the term calcium molybdate is attached is a mixture of roasted concentrate (i.e., technical-grade oxide) and ground limestone, and is used for molybdenum additions to molten steel.

Size and Characteristics of the Tungsten Industry

The tungsten-producing and -processing industry is small, diffuse, and rather specialized compared with the major nonferrous metals industries. The net domestic production figure published for 1969 was 6,500 tons of contained metal. Tungsten concentrates are produced by about 42 mines, but as coproducts of other minerals or concentrates or on an intermittent basis. The end-product forms of tungsten include the metal, the oxides, carbides, chemical forms, and ferrotungsten. The tungsten values may be transferred between plants in varying stages of refinement or form, or may be processed from mineral form to final product in a single plant.

The release of 19,000 tons of tungsten by the U.S. Government in 1969 was an unusual event in a rather diffuse industry structure, where production is erratic owing to both market conditions and the geographical and climatic (high altitude and heavy snows) conditions ruling most mine sites. No detailed analysis or prediction of future production is included in this discussion beyond the listing of recent past domestic mine production, roughly 3,500 to 5,000 tons per year. The statistics for the tungsten industry as published by the Bureau of Mines for 1965 to 1969 are given in Table 21.

TABLE 21. SALIENT TUNGSTEN STATISTICS[25]

(Thousand pounds of contained tungsten)

	1965	1966	1967	1968	1969
United States:					
Mine production	W	W	r 8,167	r 8,397	7,439
Mine shipments	7,566	r 8,482	8,649	10,188	9,405
Releases from Government stocks	926	8,273	6,393	3,225	38,314
Exports	11	101	974	623	7,152
Imports, general	3,495	4,203	2,004	1,824	1,534
Imports for consumption	3,618	4,298	1,699	1,743	1,503
Consumption of concentrate	13,868	18,058	13,860	11,038	13,053
Stocks:					
Producer	411	358	975	603	503
Consumer and dealer	1,434	1,582	1,134	574	1,066
World:					
Production	r 59,632	r 63,085	62,725	70,425	72,060
Consumption	60,634	65,441	62,628	64,778	77,227

r Revised.
W Withheld to avoid disclosing individual company confidential data.
1 Estimated tungsten content.

The most noteworthy of current tungsten mining and processing operations are listed in Table 22. In addition to the major operations shown in Table 22, intermittent tungsten production was reported for 1969 only in terms of the states of Arizona, California, Colorado, Idaho, Montana, Nevada, and Utah. No complete, current listing of tungsten-producing mines and mills is available in the literature. A survey of tungsten technology listed 21 tungsten mills in California and 27 mills in Nevada in 1959 (Table 23). The current status of production of these operations is a matter of circumstance and not readily documented.

Ferromolybdenum is also used for alloying additions of molybdenum to cast irons and steels, and is produced by either a thermite-type reaction, or in an electric furnace process. The thermite process consists of placing a charge of molybdenum oxide, aluminum, ferrosilicon, iron ore, lime, and fluorspar in a crucible and igniting the charge. The reaction is exothermic and proceeds until the iron and molybdenum are reduced to a molten state and the other components of the charge are oxidized to a slag. The slag is removed while molten, and the ferromolybdenum, after solidifying, is crushed to various sizes of lumps or powder. A higher carbon grade of ferromolybdenum is produced in an electric furnace process in which a charge of molybdic oxide, iron, coal, and lime is smelted. The different carbon and impurity-metal contents of the materials produced by the two different methods are appropriate for applications in making different grades of cast irons and steels.

Molybdenum disulfide is used as a lubricant or as an additive to lubricating oils. The disulfide used in this application is a purified form of the naturally occurring mineral molybdenite. The purified forms of molybdenum disulfide are prepared from flotation concentrates by various proprietary processes, which include such operations as screening, grinding, chemical processing, or volatilization and possibly other processes, and which produce proprietary grades of product with varying properties for different applications.

Molybdenum oxides and ammonium and sodium molybdates are the more important compounds of molybdenum and are used in pigments, chemicals, fertilizers, and glassmaking.

Given in Table 24 is a list of producers and plants which process tungsten concentrates and metal. In addition to those producers listed, there are many specialty plants which process scrap tungsten and perform metal fabrication or chemical processing as well as act as distributors of the various end products, where tungsten products are a minor portion of total production.

TABLE 22. MAJOR PRODUCERS AND PROCESSORS OF TUNGSTEN CONCENTRATES

Company	Location	Processes or Products	Major	Coproducts
Union Carbide Corp. Mining & Metals Div.	Bishop, California	Mine and mill	W	Mo, Cu, Au
Climax Molybdenum Co. (Division of AMAX[a])	Leadville, Colorado	Mine and mill	Mo	W, Sn, etc.
Ranchers Exploration and Development Corp.	Henderson, North Carolina	Mine and mill	W	
Canyon Mining Corp.	Boulder, Colorado	Mine		
Miners Exploration Co.	San Bernadino County, California	Mine and mill		
Silver Star-Queens Mines	Western Utah Gold Hill, Utah	Mine Mill		

(a) American Metal Climax, Inc.

TABLE 23. TUNGSTEN MINES AND MILLS (PAST AND/OR POSSIBLE PRODUCERS)(26)

State	County	Operations
California	Fresno	New Idria Mining and Chemical Co.
	Inyo	Round Valley Tungsten Co.
	"	El Diablo Mining Co.
	"	Red Hill Custom Mill
	"	Molybdenum Corporation of America (Beware Mill)
	"	Union Carbide Corp.
	"	Ajax Tungsten Corp.
	"	Rossi Mill
	"	Miller and Warken Mill
	"	Piute Mining and Milling Co.
	Madera	June Bee Mill
	Tulare	Tulare County Tungsten Mining Co.
	"	Sherman Peak Mining Co.
	Mono	Wah-Chang Mining Corp. (Benton Mill)
	Kern	McKee Mill
	"	Rand Mining and Milling Co.
	"	Butte Lode Mill
	San Bernadino	Surcease Mining Co.
	Ditto	Parker Bros. Mining and Milling Co.
	"	Minerals Material Co.
	"	Section 9 Tungsten Mine and Mill
Nevada	Humbolt	Getchell Mine, Inc.
	"	Winnemucca Mountain Mining Co.
	Pershing	Nevada-Massachusetts Co.
	"	Wolfram Company-Toulon Mill
	"	Trojan Mill
	Churchill	White Cap Metals Mill
	"	Churchill Tungsten Mining Company
	Douglas	Metallurgical Development Co.
	Lander	Conquest Mine and Mill
	"	Linka Mine and Mill
	White Pine	Minerva Custom Mill
	Ditto	Baltimore Camas Mill
	"	Strategic Metals - Tungstonia Mill
	Elko	White Star Tungsten Mill
	Mineral	Nevada Scheelite Corp.
	"	Dead Horse Wells Mill
	"	Kinkhead Mill
	"	Florey Mill
	"	Gun Metal Mill
	Esmeralda	Minada Corp.
	Nye	Commadore Mill
	"	Gabbs Exploration Co.
	"	El Capitan Mill
	"	Baxter Mill
	"	Yancy Custom Mill
	Lincoln	Wah Chang Corporation (Lincoln Mill)
	Clark	Tri-State Metals Mill

TABLE 24. PRODUCERS AND PROCESSORS OF TUNGSTEN MATERIALS[26,27]

Company	Location	Products or Processes
Sylvania Electric Products Inc.	Lowanda, Pennsylvania	Chemicals, metal powder, mill products
Kennametal, Inc. Nevada Scheelite Division	Hawthorne, Nevada[a] Fallow, Nevada[b]	Processing of tungsten carbide
Gulf Chemical & Metallurgical Corp.	Texas City, Texas Ironton, Ohio	Diversified smelter; tungsten metal and chemicals Calcium tungstate
Climax Molybdenum Co. (AMAX)	Colorado Coldwater, Michigan Langeloth, Pennsylvania	Mining and concentrating Processing of concentrates and compounds
Union Carbide Corporation	Pine Creek, California Niagara Falls, New York	Mining, concentrating, and processing to chemical products, ferrotungsten, metal powder
Ranchers Exploration and Development Company	North Carolina	Mining, concentrating
Adamas Carbide Corporation	Kenilworth, New Jersey	Carbide, tungsten powders
Oregon Metallurgical Corp.	Albany, Oregon	Ingot, mill product
Chem-Met Co., Inc.	Clinton, Maryland	Scheelite (from scrap)
Cleveland Refractory Metals (Division of Chase Brass & Copper Co., Inc.)	Solon, Ohio	Metal powder, mill products
Diamond Metal Alloys	Houston, Texas	Carbide powder
Fansteel, Inc.	Chicago, Illinois Baltimore, Maryland	Metal powder, mill products

Continued on following page.

TABLE 24. (continued)

Company	Location	Products or Processes
Firth Sterling	McKeesport, Pennsylvania	Carbide (metal) powder
General Electric Company Refractory Metals Division Lamp Metals and Components Dept.	Cleveland, Ohio	Mill products, powder, carbides
Kennemetal, Inc. Nevada Scheelite Division	Latrobe, Pennsylvania Fallon, Nevada	Carbide powder Carbide
M&R Refractory Metals, Inc.	Springfield, New Jersey	Metal powder and pellets
Molybdenum Corporation of America	Washington, Pennsylvania York, Pennsylvania	Ferrotungsten chemicals
Wah Chang Corporation	Glen Cove, New York	Ferrotungsten, metal chemicals
Westinghouse Electric Corp.	Blairsville, Pennsylvania	Metal forms

(a) Old plant
(b) New plant
} operations being transferred

Raw Materials and Processes[25,26,28]

Ores and Concentrating Processes

The mineral forms from which tungsten and tungsten compounds are produced are complex metal oxide forms. The mineral names and chemical nomenclature and formulas are listed in Table 25. Of the many mineral forms, only the first four are of practical significance.

TABLE 25. TUNGSTEN MINERALS

Mineral Name	Chemical Formula	Chemical Nomenclature
Scheelite	$CaWO_4$	Calcium tungstate
Feberite	$FeWO_4$	Iron tungstate
Wolframite	$(Fe, Mn)WO_4$	Iron-manganese tungstate
Hubnerite	$MnWO_4$	Manganese tungstate
Powellite	$(Ca, Mo)WO_4$	Calcium-molybdotungstate
Chillagite	$3PbWO_4 \cdot 5PbMO_4$	Lead tungstate-lead molybdate
Stolzite	$PbWO_4$	Lead tungstate
Raspite	$PbWO_4$	Lead tungstate
Cuprotungstite	$CuWO_4 \cdot 2H_2O$	Hydrous copper tungstate
Tungstite	$WO_3 \cdot H_2O$	Hydrous tungsten trioxide
Tungstenite	WS_2	Tungsten sulfide
Ferritungstite	$Fe_2O_3 \cdot WO_3 \cdot 6H_2O$	Hydrous iron-tungsten oxide

The occurrence of these minerals in workable deposits is limited to the western states mentioned previously and to isolated deposits such as the one currently worked in North Carolina and an obsolete operation in the New England area. The grades of ore currently producing tungsten are described as containing between 0.3 and 0.5 percent WO_3. This metal content is generally associated with one or more coproducts, usually molybdenum. The multiple-product nature of the ores is the feature that makes them economically practical. Tungsten concentrates generally are sold, traded, and treated at a level of 60 percent WO_3. Thus, concentration processes accomplish about the same tenfold concentration as is performed on copper ores, although the scale of operations is much smaller. The yields obtained in concentrating tungsten ores range from 60 to 90 percent, owing to the nature of the mineral particle behavior.

The concentrating or milling of tungsten ores involves the use of gravity separation methods, flotation, magnetic separation, and leaching techniques in various combinations or sometimes in series to achieve

the desired concentrate composition. The leaching and flotation operations are sometimes indirect, i.e., materials other than the tungsten compound are removed, to leave a residue with an increased proportion or percentage of tungsten.

The determinants of the design of a tungsten-concentrating operation are the minerals associated with the tungsten. The popular flotation concentration process was developed principally for sulfide ores which may be naturally or readily conditioned to be aerophilic or floatable. The common minerals of tungsten are oxide forms and are floatable only under special conditions, which may result in the simultaneous flotation of other mineral or gangue components in the ore. Each ore requires an individual process but some unique or generally common features of tungsten-concentrating processes may be identified here.

The principal considerations are that the tungstate minerals have high densities and commonly occur as coproducts with floatable sulfide minerals of other metals. The concepts of flotation are discussed in Volume I of this report and so only the broad considerations of the process are included here. Tungsten-concentration processes thus may include the usual liberation steps of crushing, grinding, classifying, and sizing which assure uniform feed of desired size to the subsequent process. If, for example, copper and/or molybdenum sulfides or iron sulfides are present in the ore, they are amenable to separation by flotation wherein the tungstate would appear in the tailing or discard portion of the flotation separation. The tungstate minerals, by virtue of a relatively high density, can be separated by gravity methods, such as table classifiers or jigs, from any lighter associated minerals. Another separation technique possible depends on the nonmagnetic nature of tungstates as opposed to the magnetic iron oxide. If the iron sulfide mineral, pyrite, or the complex iron-aluminum (or other) silicate, garnet, are present, they may be converted by roasting to forms which are magnetically separable from nonmagnetic tungstates. If the minerals apatite [$Ca_5F(PO_4)_3$] or calcite ($CaCO_3$) are present with the tungstate, they may be removed by controlled leaching with hydrochloric acid. Considerable care is necessary in leaching so that any calcium tungstate-type minerals present are not also dissolved.

Some of the elements of tungsten-concentration processes are shown in the simplified and generalized flowsheet in Figure 12. The operation of ore crushing and sizing usually involves such unit operations as primary crushing, fine crushing, and ball or rod mill grinding with associated screening, cyclones or other classifiers which pass acceptable sizes, and recycle oversize to the appropriate crushing operation. The output size of the initial sizing operation is controlled to be amenable to the subsequent operation. In the example given in the figure, the ore is conditioned initially with suitable reagents and floated to separate sulfide minerals. In the cases of many tungsten ores, an initial separation of slimes (particles less than 20 microns, for example) would be necessary. Because of the usual brittle and friable nature of tungsten minerals, slimes generation is a common occurrence during comminution

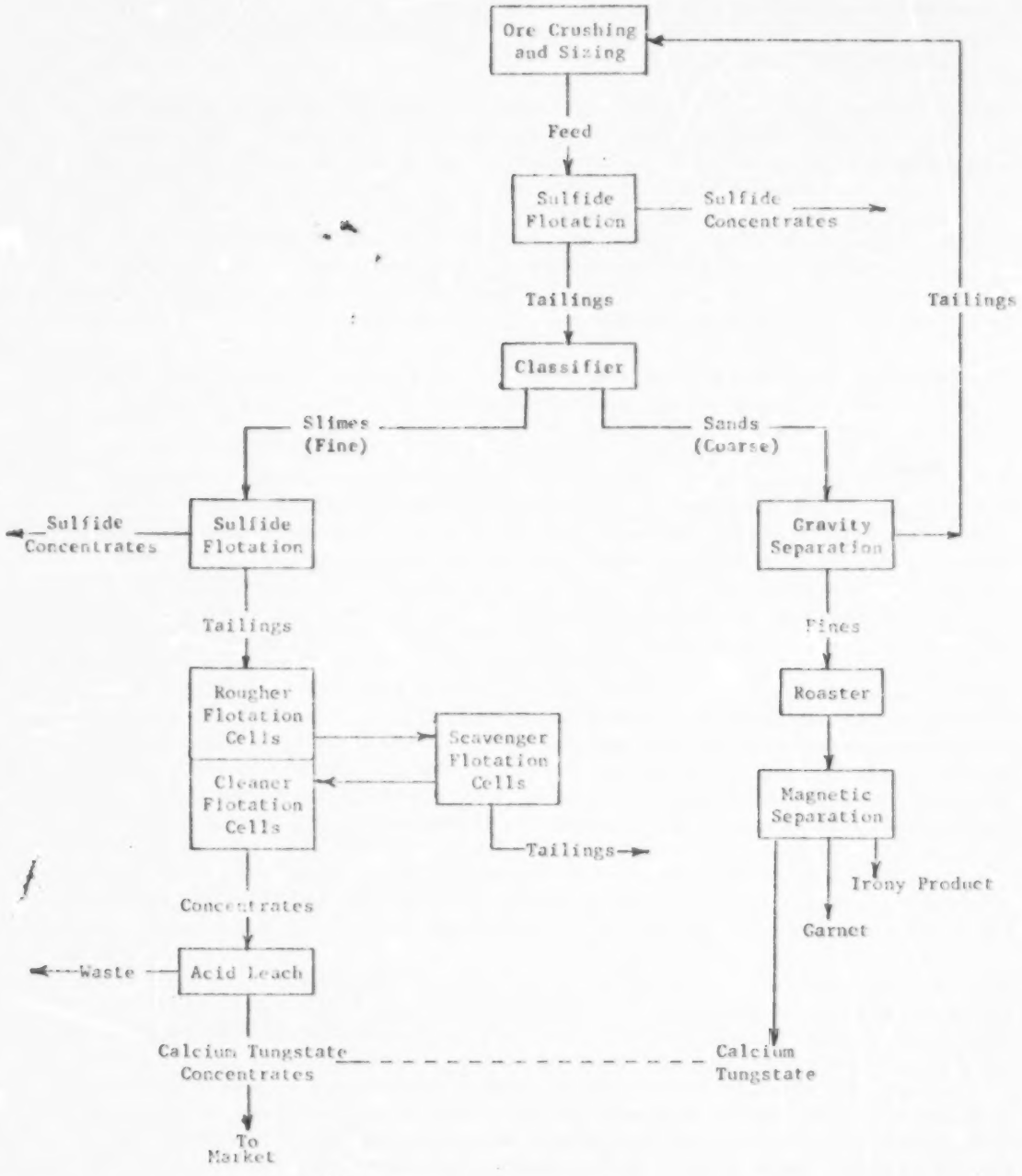

FIGURE 12. FLOWSHEET FOR PROCESSING OF TUNGSTEN ORE TO CONCENTRATES

to any size. Slimes may or may not interfere with a flotation operation but are generally detrimental to efficient separations. The indicated initial sulfide flotation could, for example, separate the coproduct sulfides of copper, molybdenum, or iron either singly by their single occurrence, or by differential flotation, or in combination, in which case the product would be treated by differential flotation for further separation. In the example, the flotation tailings are classified into fine and coarse and treated by two alternative routes. The fines are reconditioned, reagents added, and the fines refloated to achieve additional separation of sulfide minerals. After reconditioning and addition of new reagents, the fines are refloated through rougher and cleaner flotation cells, with the flotation product being in this stage the tungsten mineral and some associated gangue minerals. Components of the gangue in this example are calcite and apatite. A first-stage leach with hydrochloric acid (HCl) removes the calcite ($CaCO_3$) as a calcium chloride ($CaCl_2$) solution which is discarded. A second stage leach is used to dissolve the apatite [$CaF(PO_4)_3$], which is not dissolved in the presence of calcium chloride.

The sand fraction is further classified into two size ranges and treated with the gravity-separation technique of a reciprocating table. The large particles are returned to the beginning of the process and are subsequently and eventually processed as fines. The concentrates from the tables are dried, roasted, and subjected to magnetic separation. The magnetic separation results in a three-way split of product: a strongly magnetic high-iron-content product; a weakly magnetic product, garnet; and a nonmagnetic product, calcium tungstate. The intriguing and individual features of this particular example are that an initial crushing and grinding operation produces a product which allows the separation of sulfides by flotation and a split of the tailings into two fractions, each with a characteristic combination of gangue minerals, allowing each pair of gangue minerals to be removed, with the gravity-roast-magnetic leg screening out some of the material from the fines circuit. Acid consumption is minimized.

Treatment of Concentrates

The processing and products derived from concentrates are indicated in the chart in Figure 13. As previously discussed, the end products in the primary industry include the major categories of ferrotungsten, and scheelite, both used as additions to alloy steels, and the other categories of metallic tungsten in the forms of powder, consolidated metal, tungsten-base alloy mill products, alloying additions in superalloys, or as tungsten carbides or chemicals.

The production of ferrotungsten may use any of the types of tungsten concentrates or a mixture of them. The predominant practice in this country is the use of the electric furnace process in which the concentrates, ferrosilicon, and basic flux material (e.g., limestone) are fed

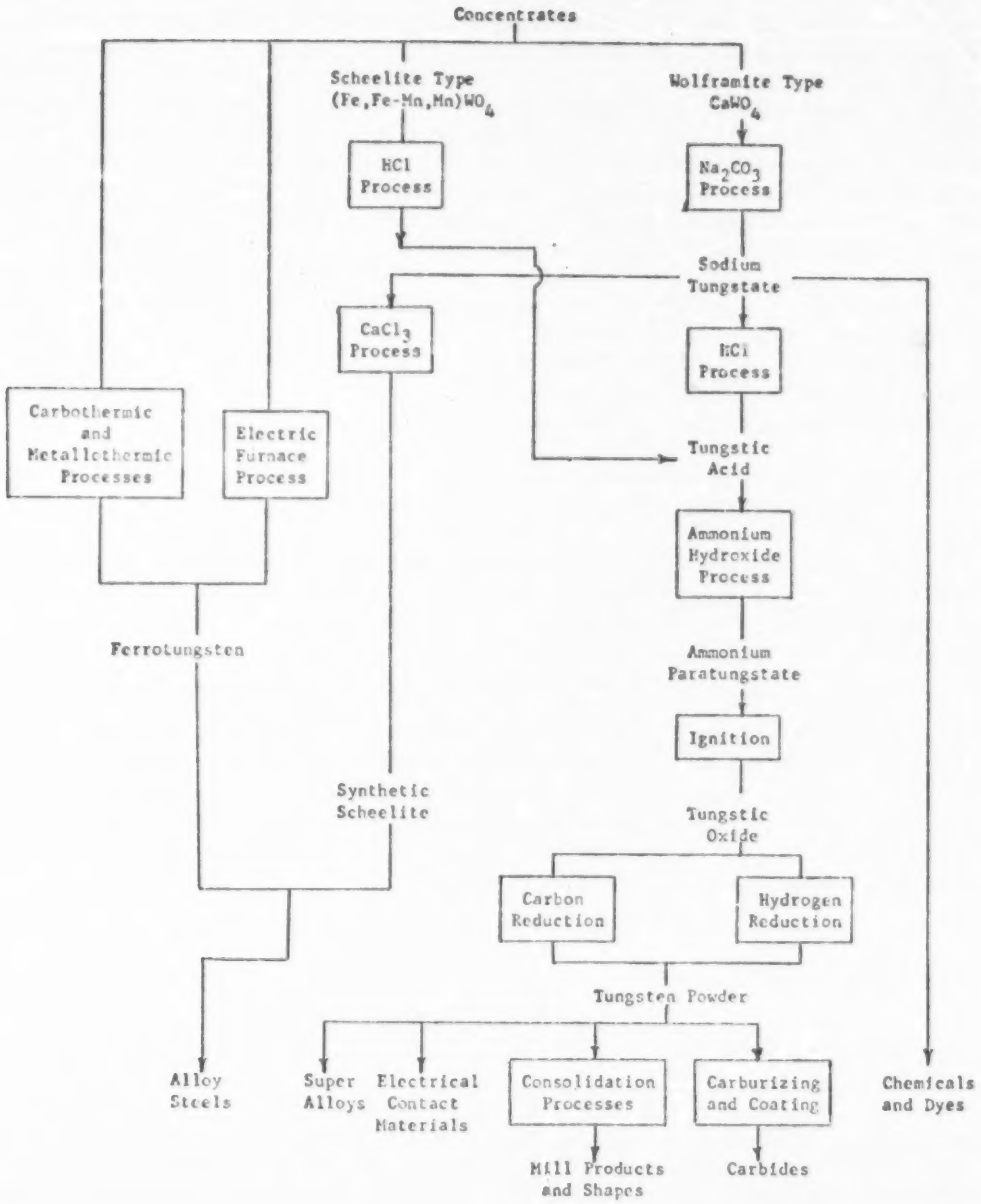

FIGURE 13. DIAGRAM OF PROCESSES AND PRODUCTS IN THE TUNGSTEN INDUSTRY

into an electric arc furnace. The mixture is smelted into a slag and a ferrotungsten product. The solid ferrotungsten may be retrieved from a demountable furnace and crushed and sold as chunks for addition to alloy steel melts.

The alternative methods of production use carbon, aluminum, or a combination of silicon and aluminum. The silicon-aluminum reaction is self-sustaining after an initial ignition, whereas the other methods of reduction are usually carried out in electric furnaces. All accomplish the reaction of a reducing agent with the oxide of tungsten in the presence of iron (either in the form of scrap steel or a ferroalloy) with the oxide products fluxed and removed as a molten slag.

Another method of adding tungsten to steels is in the form of calcium tungstate, $CaWO_4$, usually as a product called synthetic scheelite. Here the calcium tungstate reacts with the molten-steel bath so that the calcium enters the slag and the tungsten enters the molten steel as reduced metal.

The production of synthetic scheelite may utilize low-grade tungsten concentrates of the scheelite type to produce a required high-grade material usually containing about 70 percent WO_3 instead of the usual 60 percent WO_3 encountered in most concentrates. The synthetic scheelite process, indicated in simplified form in the diagram in Figure 14, consists of the selective leaching of the tungsten, followed by its precipitation and agglomeration into nodular form for addition to steel melts.

The feed material for the process consists of concentrates ranging down to about 15 percent or less WO_3. The feed is blended, ball-milled, etc., and fed as a water slurry, with the addition of sodium carbonate, to a heated, pressurized digester vessel. Heat (as steam) and pressure are applied and controlled to conditions to maximize the leaching of the tungstate as soluble sodium tungstate and to minimize the leaching of other components. The liquor from the digester is cooled in a heat exchanger and pressure filtered, including washing operations, to obtain all the solubilized tungstate. Wash waters are routed either to the subsequent process or back to the grinding circuit. The liquor is treated with various reagents to achieve the precipitation of calcium tungstate as a solid, which is filtered from the liquor and the filtrate discarded. The filter cake is dried and agglomerated in a kiln to give the final product.

The treatment of concentrates for the production of other forms of tungsten is usually started by reacting the concentrate with sodium carbonate at 800 C to achieve a fused-salt mixture, which when cooled, crushed, and water leached yields a solution of sodium tungstate. The addition of hydrochloric acid to this leach solution causes the precipitation of a solid, tungstic acid (H_3WO_4). By heating (to 1000 C) the acid is decomposed to tungsten trioxide. The preparation of a pure form of the oxide is highly desirable if pure metal powder is to be

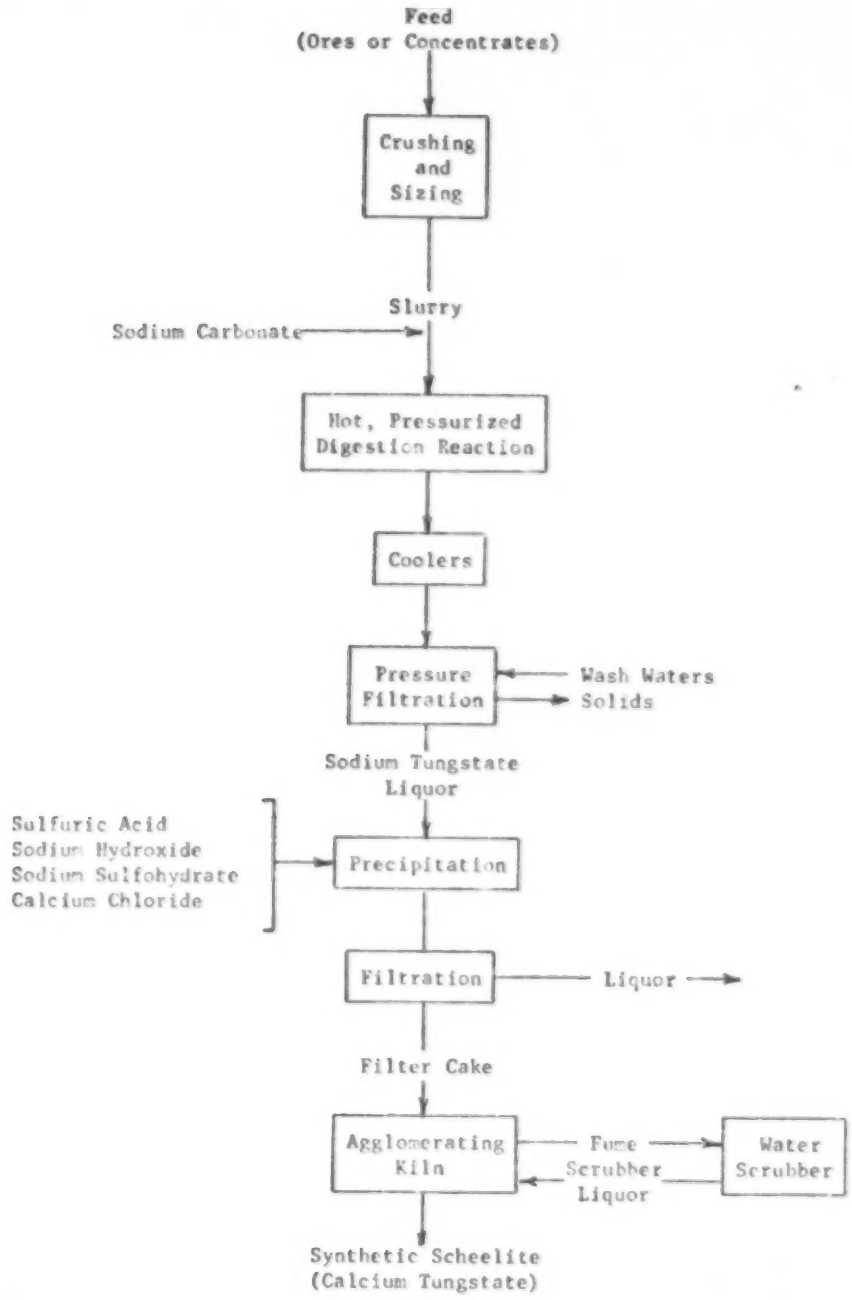

FIGURE 14. FLOWSHEET FOR THE PRODUCTION OF SYNTHETIC SCHEELITE

produced. The pure oxide may be obtained by repeated dissolving and precipitation of the tungstates as indicated in the diagram in Figure 15. Here the sodium tungstate leach liquor is treated with calcium to precipitate calcium tungstate, and the solid is filtered from the liquor. The solid is leached with HCl to produce a calcium chloride liquor and a residual solid of tungstic acid, H_3WO_4. After washing and separation, the solid tungstic acid is redissolved in ammonium hydroxide, the solution filtered, and solid impurities discarded. The clarified solution (ammonium paratungstate) is treated with hydrochloric acid to reprecipitate tungstic acid, with the liquor being discarded after the separation of the solid. The solids are redissolved in ammonium hydroxide and reprecipitated with additional impurities remaining in the discarded liquor. The solid tungstic acid, H_3WO_4, is dried and heated or ignited to decompose to the trioxide (WO_3) and water vapor.

The point of the above purification steps is to achieve high-purity oxide and remove a number of impurities usually found in the ores: iron, manganese, calcium, molybdenum, alumina, silica, lead, copper, titanium, sulfur, phosphorus, arsenic, antimony, bismuth, and tin.

Pure tungstic oxide is used for the production of tungsten-metal powder. Most commonly the process consists of charging the oxide in ceramic containers, or "boats", into a furnace and heating under a circulating hydrogen atmosphere. Furnace temperatures usually are about 1200 C, where the overall reaction proceeds.

$$WO_3 + 3H_2 \rightarrow W + 3H_2O.$$

Because of its high melting point, and rapid oxidation rate, tungsten-metal powders are treated by powder-metallurgy techniques with protective or inert atmospheres or in vacuum furnaces. The production of metal parts or shapes proceeds through the steps of hot or cold compaction of powders, sintering, and hot or cold deformation to accomplish the consolidation and shaping of the metal. The consolidation of tungsten is also achieved by the cold-crucible, arc-melting techniques described in the section of this report describing the processing of molybdenum. Tungsten metal end products include sintered, porous electrical contacts, sintered electrical contacts in which the porous tungsten skeleton is filled or infiltrated with copper or silver, and consolidated tungsten mill products such as plate, bar, rod, wire, foil, etc. The classical application of tungsten wire is, of course, in lamp filaments. The applications of tungsten and tungsten-base alloys are determined by its density, high-temperature strength, and high oxidation rate, the last requiring that its high-temperature service be in nonoxidizing (i.e., inert gas or vacuum) environments.

The production of tungsten carbide involves the heating of oxide or metal powder mixed with powdered carbon. If the oxide is used, the carbon reduces the oxide to the metal. The carbon and tungsten interact at high temperatures by solid-state diffusion to form the carbide compounds WC and W_2C. Cemented carbides are produced by ball milling a

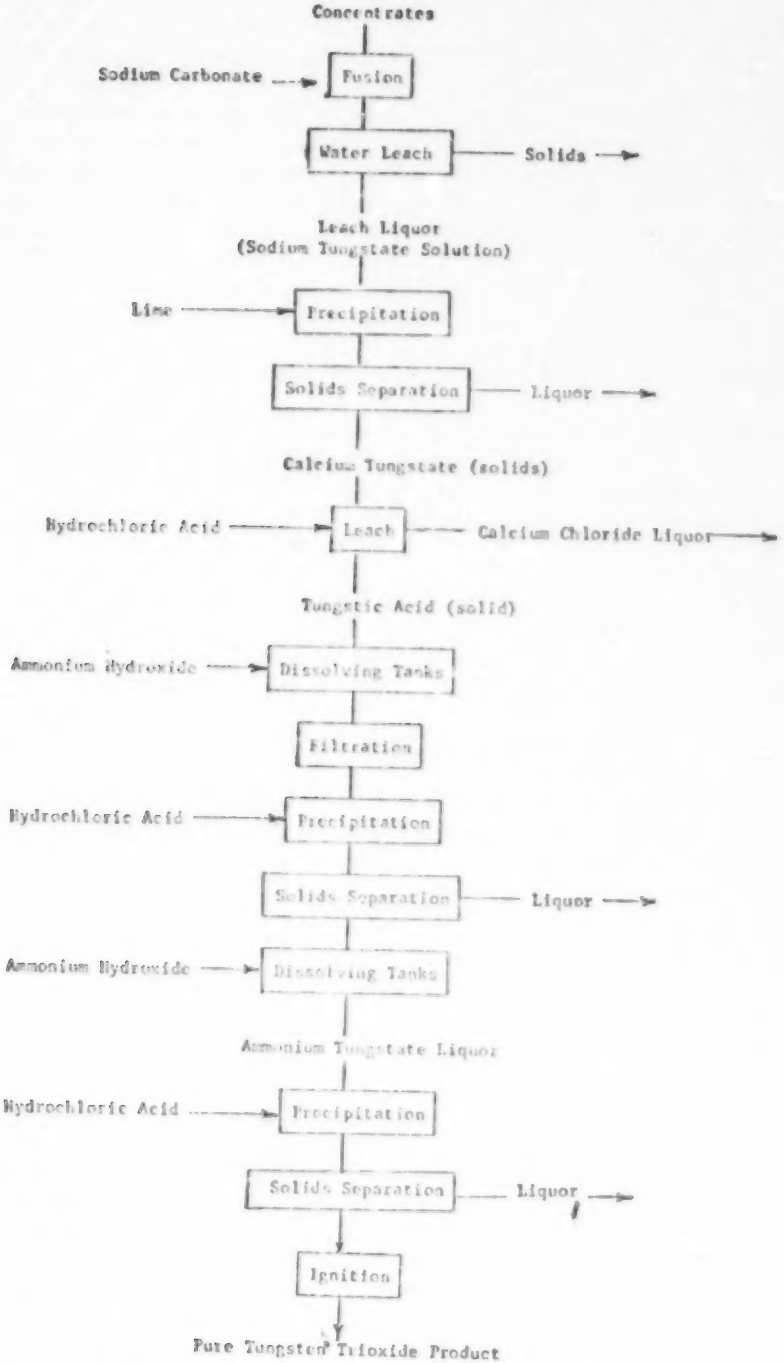

FIGURE 15. FLOWSHEET FOR THE PURIFICATION OF TUNGSTEN TRIOXIDE

mixture of carbide powders and metal (usually cobalt) powder to coat each carbide particle with the metal, after which hot- or cold-pressing and sintering operations produce a bonding of the particles by means of the adhering metal. With the technique of the modern arc furnace, carbides may be fused and cast into simple shapes. Carbides are used for applications such as cutting and grinding tools, engine components such as valves, and abrasion-resistant parts in sand-blasting machines or rocket engines.

Water Practices in the Molybdenum and Tungsten Industries

Water usage in the molybdenum- and tungsten-producing industries shows a considerable number of components in view of the great number of various unit processes. Water-use data were obtained from only four operations in this segment of industry. However, the data are reviewed here to serve as examples of what may be expected as regards waste water from such plant operations.

The refractory-metal industry may be considered from the viewpoint of plant operation and water usage to consist of two segments: mining and milling, and the chemical-type plant in which concentrates are processed to chemical or metal end products.

Mining and milling of the metal ores represents a somewhat complex situation in the case of molybdenum and tungsten. Because of the coproduct status of molybdenum minerals, a considerable portion of water usage attributable to the mining and milling of molybdenum is initially discussed in Volume I of this report, under the discussion of the mining and concentration of copper ores.

In the case of the major molybdenum producers, the published literature serves as a source of information on individual problems and water-pollution-control practices associated with specific molybdenum mining operations.

In 1966, work on the effects and control of tailings-pond effluent from a flotation-concentrating operation included cooperative studies by industry and state officials.[29] A molybdenum mining and concentrating operation was found, by virtue of breakdown of some elements of the plant, to be leaking concentrator effluents from points other than the originally designed tailings-pond discharge point, resulting in fish kills in the receiving river. The breakdowns consisted of breaks in pipe lines carrying the slurry from the concentrator to the tailings pond and in a break in conduit under the tailings pond.

The breaks in the pipe line were traced to the abrasive wear of the steel pipe by the crushed rock waste in the tailings slurry, and were found most often at curves or bends in the pipe line.

This aspect of the problem has been minimized by constant patrol and inspection of the pipe line, using test devices to check the thickness of the pipe. The break in the underground conduit was attributed to the shifting of the fill on which the conduit was originally laid. The conduit was lined with steel pipe to overcome the leakage problem.

One of the major parts of this work was the examination of the disposition of the reagents used in the concentration process, and some modification of reagent use, involving the use of minimum quantities of reagents so that no excess is discharged in the effluent. Some of the most interesting information generated by this study is given in the following tables. The first (Table 26) gives information on the nature and disposition of the flotation reagents, while the second (Table 27) shows the published data on waste analyses.

The conclusions of the article were that with proper control of reagent additions, a tailings-pond effluent has been achieved which is of sufficient quality that fingerling trout survive indefinitely in the undiluted effluent.

Still other published information has indicated the approach to water-pollution-control practice in a new molybdenum mining and concentrating operation.[30,31] This operation, relatively recent in being started, has had the benefit of advance consideration of effects on the environment. While complete details of the operation of the metallurgical processes have not yet been published, some of the major considerations for control of water pollution have been identified. Most simply stated, the plant and associated natural and new drainage and water systems have been designed to isolate the plant water system from the surroundings in case of equipment failure or floods up to a level of the largest expectable flood in a period of 100 years. The concentrator and tailings disposal area were placed within the features of the local terrain to allow for natural drainage of spills or leaks into the tailings pond, with the only possible discharge being completely controlled. To prevent storm runoff entering and overloading the controlled system, cut-off drainage measures were installed to route any such natural drainage around the operation to be discharged to local streams without entering the mill system.

Included in this design are collection systems to control mine drainage water and basins and dams below the tailings pond to serve the purpose of collecting any potential underground seepage escaping from the tailings storage area and moving down the local geological system. This system also allows for extensive recirculation and reuse of water in the concentrating operation.

Water Usage in Metal-Processing Plants

The water-usage patterns exhibited by metal-processing plants exhibited

TABLE 26. REAGENTS USED IN FLOTATION OF MOLYBDENITE[29]

Reagent	Chemical Composition	Function	Reagent Amount Added (lb/ton ore)	#/Ton Water	Effect
TEB or alternate	1, 1, 3, Triethoxy butane	Frother-collector	0.05	0.03	largely complexed with MoS_2 concentrates very small amount remaining in tailings water
Pine Oil	Mixed aromatic alcohols	Frother-collector	0.04	0.03	
Aeroflot 3302	Xanthate ester	Promoter	0.007	0.005	completely consumed by MoS_2 concentrates as insoluble coatings on mineral surfaces.
Texaco Vapor Oil 1527	Saturated hydrocarbons	Collector	0.12	0.08	
Pyramid Diesel Fuel	Saturated hydrocarbons	Collector	0.05	0.03	
"N" Silicate	Na_2SiO_3(Na_2O:SiO_2 = 1:3.2)	Dispersant	0.20	0.13	mostly complexed with gangue slimes
Phosphorous pentasulfide	P_2S_5	Depressant	0.06	0.04	completely consumed by gangue
Sodium sulfide	Na_2S	Depressant	0.08	0.05	sulfides as insoluble coatings on surfaces
Sodium hydroxide	NaOH	Depressant	0.10	0.07	OH^- ions partially adsorbed on the gangue sulfide surfaces. Na^+ ions remaining in water
Milk of Lime	$Ca(OH)_2$	pH modifier	0.30	0.20	
Sodium cyanide	NaCN	Depressant	0.005	0.003	CN^- complexed with gangue sulfides or completely oxidized to thiocyanate in tailings. No free CN^- left in water
Potassium permanganate	$KMnO_4$	Modifier	0.003	0.002	used up as an oxidizer, MnO_2 as end product
Superfloc 127	Water soluble polyacrylamid	Flocculant	0.008	0.005	consumed by gangue slimes, very little left in water

TABLE 27. ANALYSIS OF WATER SAMPLES[29]

(All values in mg/l)

	River Above Outfall	River Below Outfall	Tailing Pond Pool	Reclaim Water	Fag Cleaner Tailing	Total Tailing
CN	N.D.	N.D.	N.D.	<0.005	N.D.	<0.005
SCN	N.D.	0.002	0.007	0.119	0.020	0.100
$Fe(CN)_6$	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
S	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
P	N.D.	N D.	N.D.	<0.01	N.D.	<0.01
Mo	O	O	6.90	2.93	5.40	3.78
Fe	<0.05	<0.05	<0.05	0.17	0.35	<0.05
Cu	<0.01	<0.01	0.03	0.01	0.01	0.01
Pb	0.08	<0.05	0.18	0.10	0.10	0.07
Zn	0.037	0.022	0.015	0.054	0.055	0.015
Mn	0.15	0.15	0.95	0.90	0.73	0.50
Ca	31.0	30.6	122.	65.1	77.1	71.1
Mg	6.0	7.0	24.0	16.0	17.0	17.6

N.D. - none detected

general characteristics apparently governed by two general conditions: municipal locations and the relatively high price of the materials being processed. These factors corresponded to generally good knowledge and control of water systems and the use of processes and waste-water treatments to control material losses. The major common features of the refractory-metal-processing plants, as reported during this study, are indicated by the generalized water-use diagram in Figure 16. The sources for these plants were municipal water systems, and with the exception of one plant's boiler feed water, no treatment was applied to incoming water. The uses of the water included the usual common categories of sanitation, cooling, boiler feed, and in the cases of two of the four plants, air-pollution control. The process-water category included uses in acid leaching and other chemical operations, the washing and rinsing of the metal products, and use in open coolant and lubricant circuits in metals fabrication, machining, and grinding operations. In addition, one plant reported use and control of water in a cyanide equipment washing operation.

The receivers of discharge waters of these plants included sanitary sewers, storm sewers, and surface waters. The discharge patterns generally showed segregation of waste-water streams, with neutralization or other treatment before release of waste water from specific operations.

The water-usage data reported by these plants is given in Table 28. Total intakes for the plants vary considerably and merely reflect that plant size and operations are considerably diverse. However, the figures show considerable use of water in these complex processing plants. The percentages of water used for the various categories within the plant (Table 29) show that the two categories of process and cooling are the major ones in these plants.

Waste-Water Sources, Treatment, Practices, and Costs

Of the four plants submitting data, the quantities of discharge water fell into the following categories:

	Million Gal/Yr
Total Discharge	305.7
Sanitary Waste Water	18.6
Industrial Waste Water	
Treated	105.8
Untreated	181.3

All of the sanitary waste waters of these plants were discharged to municipal sanitary sewers. The industrial waste waters were discharged to sanitary sewers, storm sewers, or surface waters. Only one of the plants indicated any problem with discharge-waste-water quality and

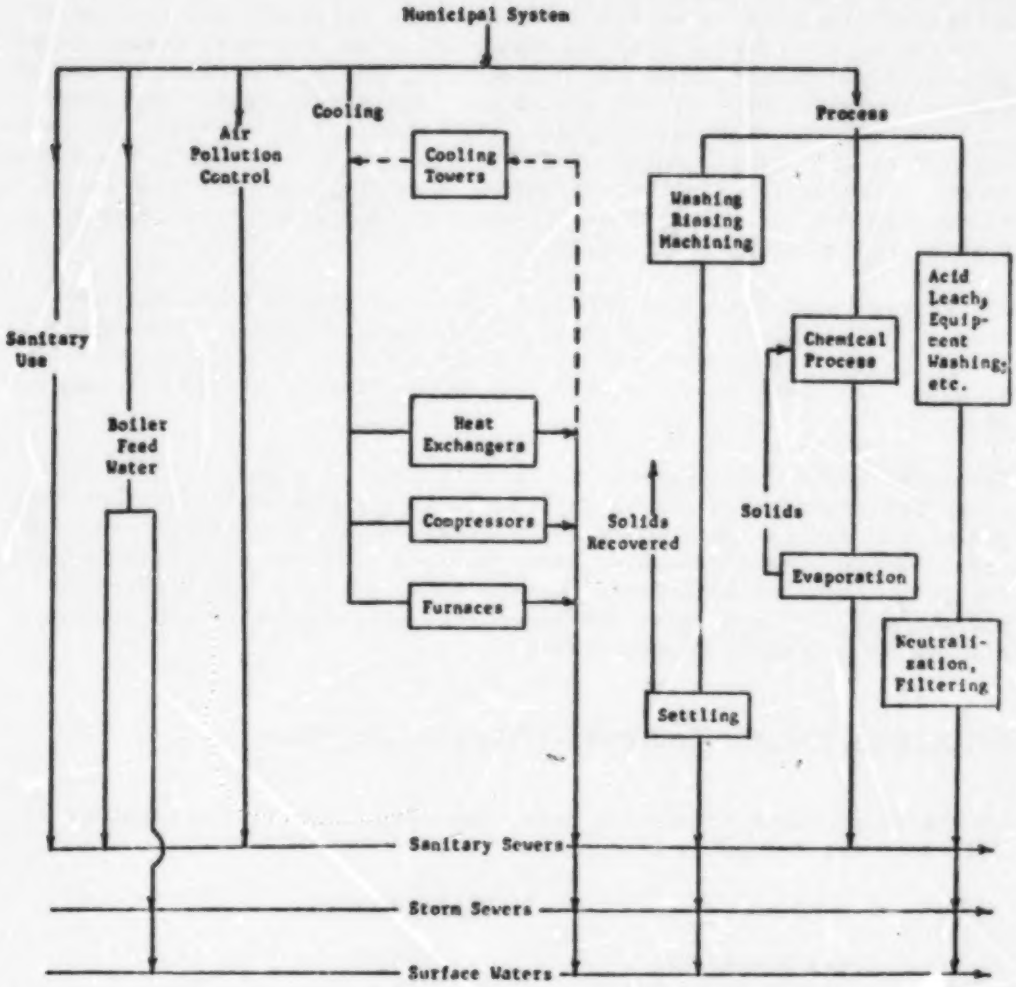

FIGURE 16. CHARACTERISTICS OF WATER CIRCUITS OF MOLYBDENUM AND TUNGSTEN PROCESSING PLANTS

TABLE 28. WATER DATA FOR REFRACTORY-METAL-PROCESSING PLANTS

Total Water Intake, MGY[a]	Discharge to Receiving Waters, MGY	Total Water Use, New and Recirculated, MGY	Water Intake per Ton of Metal, gal	Water Used per Ton of Metal, gal	Consumption (Intake minus Discharge) per Ton of Metal, gal
40.0	29.0	40.0	42,200	42,200	3,544
16.7	11.7	27.5	111,000	183,000	33,000
270.	255	NA	NA	NA	NA
22.9	>10	284	196,000	2,430,000	NA

(a) Million gallons per year.

TABLE 29. WATER USES AND RECIRCULATION PRACTICE IN REFRACTORY METAL PROCESSING PLANTS

Percent of New Water Intake						Use Ratio[a] by Process						
Process	Cooling	Boiler Feed	Air Pollution Control	Sanitary	Other	Process	Cooling	Boiler Feed	Air Pollution Control	Sanitary	Other	Overall Use Ratio
90.6	--	6.3	--	3.1	--	0	0	0	0	0	0	1
20.0	65.0	--	5.0	--	10.0	1	2	--	1	--	1	1.6
52.9	17.6	23.5	--	5.9	--	--	--	--	--	--	--	>1[b]
28.4	67.6	--	--	4.0	--	1	18.5	--	--	--	1	12.9

(a) Use Ratio = Total Use ÷ New Water Use; 1 signifies no recycling.

(b) Recirculation reported but not specified.

identified heavy metals content as the problem, with the receiver being surface water. The water treated by these plants was all of the type identified as waste water from acid-leaching operations and was all treated by neutralization and filtration. Lime and sodium carbonate were used as neutralizing reagents.

Within the category of untreated water reported above, the respondents included washing, rinsing, and machining coolants, which were actually treated by simple settling. By the definition used in this report, the water is classified as process water since it contacts the product. However, the respondents stated that none of the processed refractory metals entered this type of water. The settling out of the inert metal particles was classed as a materials-recovery measure by these plants, as was the recycling of some of the neutralization sludges. One plant reported better than 99 percent yield of processed material, which would be understandable in view of the value of refractory metals relative to other metals.

One characteristic of these plants is indicated in the water-use diagram in Figure 16. In three of the four plants, water use was segregated and waste-water streams were directed to specific receivers. Examples of this included the splitting of streams of used cooling and process water, partly to sanitary sewers and partly to storm sewers.

Only two types of water costs were reported in this segment of industry. A cost of $0.43 per 1000 gallons was given for the neutralization and vacuum filtration of acid-leaching waste water. Total water costs for both municipal supply and sewer rates were reported as $0.37 and $0.57 per 1000 gallons of intake, although sewer rates were included in the charges. In the plant with the lower rate, some recirculation was practiced, but not to a large extent. In the plant with the higher rate of water cost, extensive evaporation was practiced (with associated materials recovery), and one extensive cooling-water circuit was segregated with its own reservoir and a discharge of carefully monitored water to natural surface water.

SECTION IX

DISCUSSION

A number of nonferrous metals producing industries, processes and associated water usage and water pollution control practices have been discussed in this report.

The content of this volume has been reviewed and assessed in terms of unit processes and associated waste waters. The numerous unit processes covered have led to a tabular arrangement in presenting this assessment, which is given in the form of Table 30.

The approach has been to review each metal in terms of all unit processes, indicate whether water is used and follow with waste water characteristic and control status, wherever such information was obtained in the program. Also included are recommendations for the next action appropriate for each process step indicated.

The data presented in Table 30 indicate that there are many specialized problems but a brief discussion may aid in the understanding of the table entries. The recommendations are in terms of double objectives: (1) identifying needs for research development, or demonstration to lend impetus to water quality improvement, and (2) assessing the approach of the study to the point where unit process waste loads and effluent standards standards could be set. There follow some generalizations which may be drawn from the table.

The hot caustic leaching process by which bauxite ore is treated to produce refined alumina, and the fused salt electrolysis process by which alumina is smelted to aluminum metal were discussed in the review of the aluminum industry. Alumina refineries show no discharge of process (i.e., caustic) liquors, the process being characterized by closed vessels and extensive evaporation processes which conserve the process materials. Rather, the alumina refineries were characterized by a closed water circuit (i.e., zero discharge), with the major feature being the recirculation of water from a red-mud lake where ore residue is accumulated. The waste waters identified by this study for a small fraction of the alumina refineries surveyed were of the types common to many industries: cooling tower blowdown, boiler water bleed-off, sanitary wastes, and miscellaneous water treatment waste streams. The overall trend in the information obtained was toward decreased or zero discharge.

Aluminum smelters show the same trend. At smelters, the classical major use of water has been for air pollution control devices to control the fluoride and carbonaceous fume from the electrolytic cells. The overall trend in smelters is influenced by two factors: materials

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TABLE 30. ASSESSMENT OF INFORMATION OBTAINED IN TERMS OF UNIT PROCESSES AND FUTURE NEEDS

Metal	Nominal or Overall Operation	Unit Operation or Process	Category or Use of Water	Waste Water Characteristics	Assessment of Reported Status of Waste Water Treatment or Water Pollution Control	Recommended Future Action
Aluminum	Mining	Mining			Two operating sites in Arkansas no information	Need basic information; maybe best handled at state level.
	Bauxite ore refining; alumina refining	Steam plant, calcining, furnace cooling	Indirect cooling	As previously		As above
		Caustic leaching	Process	Red mud slurry; possible high pH, very high suspended solids.	Mostly lagooned (red mud lake) and recycled; one or more cases involve direct discharge; recycle rate generally high in the industry, no specific needs identified.	This problem of dewatering and solid waste disposal is being studied by U.S. Bureau of Mines.
Aluminum	Smelting	Rectifiers, Melting furnaces	Indirect cooling	As previously		As above
		Metal casting	Direct cooling	As previously		As above
		Anode plant Gas scrubbers	Process	Carbonaceous suspended solids; dissolved volatile hydrocarbons, oils, tar, sulfur oxides.	Currently skimmed, settled and diluted for release; better treatments need development.	Need R&D for water treatment process; need additional analyses to set waste loads, economic, and effluent standards on current state of the art.
		Pot line gas scrubbers	Process	High fluoride, chloride, sodium, aluminum, and sulfate ions.	Recovery and recycle practiced in some cases; but process should be optimized, as should the treatment of necessary small bleed-off streams from recovery operations. The impact of a proprietary dry fume-scrubbing method should be assessed.	Need additional analyses to set waste loads etc. Need R&D for fluoride recovery process efficiency.
Mercury	Mining	Mining	Mine drainage	High dissolved salts; potentially high mercury	Impact uncertain due to remote locations and arid climate conditions; information sample poor due to industry air pollution/economic status.	Suggest watchdog-type exercise to continually assess industry as operations fluctuate; the number of operations is currently decreasing, due to price situation.

TABLE 30. (continued)

Metal	Nominal or Overall Operation	Unit Operation or Process	Category or Use of Water	Waste Water Characteristics	Assessment of Reported Status of Waste Water Treatment or Water Pollution Control	Recommended Future Action
Mercury	Furnacing	Condenser scale and washdown	Process	Mercury and soot contents	One example gave settling and percolation through slag dump.	See above
	Overall	--	--	--	Air pollution problems would possibly result in process changes with water pollution potential.	
Gold	Placer mining	Dredging			No information	Need basic industry data and problem definition.
		Washing and screening			No information	Need basic industry data and problem definition.
		Gravity concentration			No information	Need basic industry data and problem definition.
	Lode mining	Underground mining	Mine drainage		No information	Need basic industry data and problem definition.
		Gravity concentration	Process		No information	Need basic industry data and problem definition.
Gold	Extraction	Amalgamation	Process	Suspended solids (high slimes), high mercury	One instance showed amalgamation discontinued; information incomplete.	Need basic information on number of industrial operations and feasibility of alternative extraction processes.
	Extraction	Cyanide leaching	Process	Suspended solids (high slimes), high cyanide	One case deciding between oxidation in holding ponds or destruction with hypochlorite; information incomplete.	Need better basic information on industry practice or the leading example could be used to set waste loads, costs, and effluent standards on the basis of holding pond oxidation of cyanides to cyanates.
	Refining	Doré-furnace	Indirect cooling	As previously	Information lacking	Need basic information on industrial practice for problem definition.
	Refining	Parting plant	Electrolytic chloride solutions	Unknown		
Silver	Mining	--		--	There are 4 nominal silver mines in the U.S. (the balance of silver is mined at copper, lead, and zinc mines); information lacking on the 4 silver mines.	Need basic information on four operations.
	Concentration and extraction			--	Information lacking for the four silver mines.	Same

TABLE 30. (continued)

Metal	Nominal or Overall Operation	Unit Operation or Process	Category or Use of Water	Waste Water Characteristics	Assessment of Reported Status of Waste Water Treatment or Water Pollution Control	Recommended Future Action
	Refining	Dore furnace, parting plant	Cooling electrolyte	--	Information lacking for the output of the four silver mines.	Same
Molybdenum	Mining	Mining	--	--	One of two molybdenum mines is constructing a total drainage control system.	No action recommended
	Concentration	Froth flotation	Process	High suspended solids, high cyanides	One of two molybdenum concentrators has developed use of very low cyanides in flotation to remedy pollution problems.	
	Extraction	Roasting			Potential SO_x air pollution problem may become a water pollution problem by virtue of wet gas scrubbing.	May be studied as portion of acid plant water disposal problem, as encountered in copper, lead, and zinc industries
		Hydrogen reduction and powder processing	Powder washing	Spent acid leachants, waste chemical solutions	Well controlled by evaporation or neutralization and filtering, in cases surveyed, due to high value of recovered material; wastes controlled included cyanide components.	No action recommended
Tungsten	Mining, concentration	Flotation or gravity concentration	Mine Drainage	--	Information lacking	Basic information needed
			Process	--	Information lacking; mine-concentrator operations usually at high altitudes and remote locations; operations intermittent due to heavy snows and fluctuating prices.	Basic information needed
	Metal reduction	Pyrometallurgical	--	--	Information lacking; probably indirect cooling water would be major water use; air pollution control may produce sludges.	Basic information needed
	Scheelite (Tungstic oxide) production	Acid leaching and precipitation	Process	Possible high chlorides and low pH	Information lacking; potential problem	Basic information needed
	Metal powder production and processing	Hydrogen reduction	--	--	Similar to that for molybdenum above; high metal value results in careful control in those cases surveyed.	No action recommended

TABLE 30. (continued)

Metal	Nominal or Overall Operation	Unit Operation or Process	Category or Use of Water	Waste Water Characteristics	Assessment of Reported Status of Waste Water Treatment or Water Pollution Control	Recommended Future Action
Tungsten		Metal consolidation			Indirect cooling water appears to be major use; machining waste water treated for materials recovery.	
Vanadium (not included in report)			Recent developments include an inference in a water study report from Arkansas that high chlorides in lake water are attributable to one of the two major vanadium-producing plants in the U.S.; the other major plant is in Colorado, where a chloride, air-pollution problem may exist; this may become a water problem via the wet-scrubber route.			Too few plant operations to reach firm recommendations.

recovery from the wet scrubbing operation and the advent of a new dry scrubbing system which also recovers fume components. The major trends identified were decreasing discharges of waste water associated with a rapid expansion of smelting capacity. The only research and development needs identified in the aluminum industry were process development for the removal or recovery of fluoride type components in wet scrubbing liquors.

The current situation and processes of the primary mercury industry reflected considerable uncertainty regarding future needs. The primary mercury industry shows continued contraction due to simultaneous pressures of market economics and air pollution controls. Water pollution control practices of a very small sample of producers were mostly indicative of remote locations and arduous climates. The waste water characteristics reported showed only elevated values of salts and some metals. No specific needs were identified at this time. The future of primary mercury producers will most likely contain some increased control of air emissions. It can only be speculated that one approach to the air emissions problem would be the initiation of hydrometallurgical operations (e.g., leaching with sodium sulfide or hypochlorite solutions). If such processes, whose feasibility remain to be demonstrated, were to be initiated, the requisite water pollution control measures could be designed into the new installations.

The review of the primary gold and silver industries indicated a similar current decrease in the number of operations. The information available indicated that operations in desert areas showed zero discharge and high recirculation of water similar to the circumstances of mining and concentrating operations discussed in Volume I of this report. In contrast, the largest gold mine in the United States has reduced mercury in its discharge water to zero by suspending the use of the classic amalgamation process and is currently dealing with the remaining problem of cyanide in waste waters.

The primary molybdenum industry has published documentation of two approaches to water pollution control: one included the initiation of special surveillance and water control measures to prevent accidental discharges of tailings slurry and modification of reagent concentration in a flotation process; the other demonstrated approach was the design of water pollution control measures into an extensive mine and concentrator operation. The design approach was to isolate the entire operation from incoming drainage and to allow for complete fail-safe type control of all process water, accidental spills, mine drainage, and underground seepage.

The primary tungsten industry, which utilizes both flotation and acid leaching processes for the concentration of ores, remains largely unknown in terms of this study. Plants processing the tungsten concentrates to various end products were associated with municipal water systems and showed high materials recovery (i.e., close control of processing water) and generally showed careful segregation of waste water

streams. One such plant indicated a need for control of heavy metals content in process waste water and indicated a desire to achieve associated materials recovery.

SECTION X

ACKNOWLEDGMENT

The sections of this report dealing with waste-water sources, characteristics, amounts, and treatment practices are based largely on the contributions of data and information of producers of nonferrous metals. These contributions were made on a purely voluntary basis and at no cost to the project. The constraint of confidentiality does not allow the recognition of the contributors to this study on an individual or corporate basis, thus due acknowledgment must be given to the nonferrous metals industry in general.

Acknowledgment can be given to the American Mining Congress Ad Hoc Committee on Wastewater Treatment Practice Survey. This committee served to establish policies, supply information, and contribute expert technical review and comment on various sections of this report.

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SECTION XI

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